



THIRD SEMI-ANNUAL TECHNICAL REPORT

August 1, 1971 -- January 31, 1972

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NEW SUPERCONDUCTORS

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13. ABSTRACT This report covers work on the study of possible high temperature superconductors. It describes theoretical work on filamentary organo-metallic materials - the conduction mechanism, band theory and screening; progress towards the synthesis of metallic chain compounds and related organo-metallic complexes, and experimental studies of their solid state properties.		

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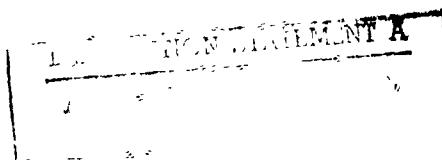
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I. INTRODUCTION

The objective of this program is to study the theoretical and synthetic problems of obtaining novel superconducting materials with high transition temperatures. It is based on the hope that higher transition temperatures can be obtained through the use of the excitonic interaction in a superconductor instead of the well understood phonon interaction. From studies of known compounds we expect to be able to estimate whether or not the excitonic interaction in related structures could be strong enough to lead to the superconducting state. The nature of the problem requires an interdisciplinary approach, hence the program is divided into several sections; a theoretical section concerned with calculations of the various interactions, screening and band structure; a synthetic section involved in the synthesis of organo-metallic polymers and dye-chelate metal complexes; an X-ray section for determining the structure of crystalline samples; and finally an experimental section for studying the properties of the prepared materials.

In the past six months substantial progress has been made in understanding one of the principle classes of organo-metallic linear chain compounds which we have been studying. These are the Krogmann salts whose conductivity we find can be well described by a Mott type variable range hopping mechanism. This type of conductivity is characterized by a temperature dependence given by $\log \sigma \approx T^{-\frac{1}{2}}$. It arises in such one dimensional systems from the random field at the chain sites due to disorder in some feature of the chain.

Good progress has also been made in calculating the degree of screening which occurs in these filamentary materials. It should now be possible to make more realistic calculations of the electron-electron interaction between electrons on the linear chains. Work has just started on applying these screening calculations to this problem.

II. THEORETICAL PROGRAM

Several different problems have been studied in this section. Because of the special importance of the linear chain Krogmann type salts as possible prototype materials for a high T_c superconductor, considerable effort was devoted to attempting to get a better understanding of the mechanism of conductivity in these materials.

As stressed in the previous report the magnitude of the screening of the Coulomb field plays a critical role in determining whether or not the excitonic interaction could yield a net attractive interaction. For this reason a considerable effort was devoted to this problem. The results are now ready to be applied to calculation of the effective interaction.

Work has continued on the multiple scattering technique for calculating the band structure of the linear chain systems and, in its molecular form, for determining the properties of the transition metal complexes.

Conductivity Mechanism in the Krogmann Salts - W. A. Little

As discussed in the previous report (pg. 105) measurements of the thermoelectric power of $\text{Ir}(\text{CO})_{2.9}\text{Br}_{1.1}$ gave the surprising result indicating a thermally activated mobility with a temperature independent carrier density. This suggested that the conductivity of this partially oxidized Krogmann compound was dominated by a hopping mechanism. Furthermore, in this and the other Krogmann compounds there is always present some degree of disorder. The Iridium compound may be considered as a disordered mixture of $\text{Ir}(\text{CO})_2\text{Br}_2$ and $\text{Ir}(\text{CO})_3\text{Br}$; while $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3} \cdot n\text{H}_2\text{O}$ as a random mixture of $\text{K}_2\text{Pt}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$ and $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_2$. It is known from the work of R. E. Borland (Proc. Phys. Soc. 73, 926 (1961)) and N. F. Mott and W. D. Twose (Adv. Phys. 10, 107 (1961)) that in a disordered one-dimensional system the electron states are localized.

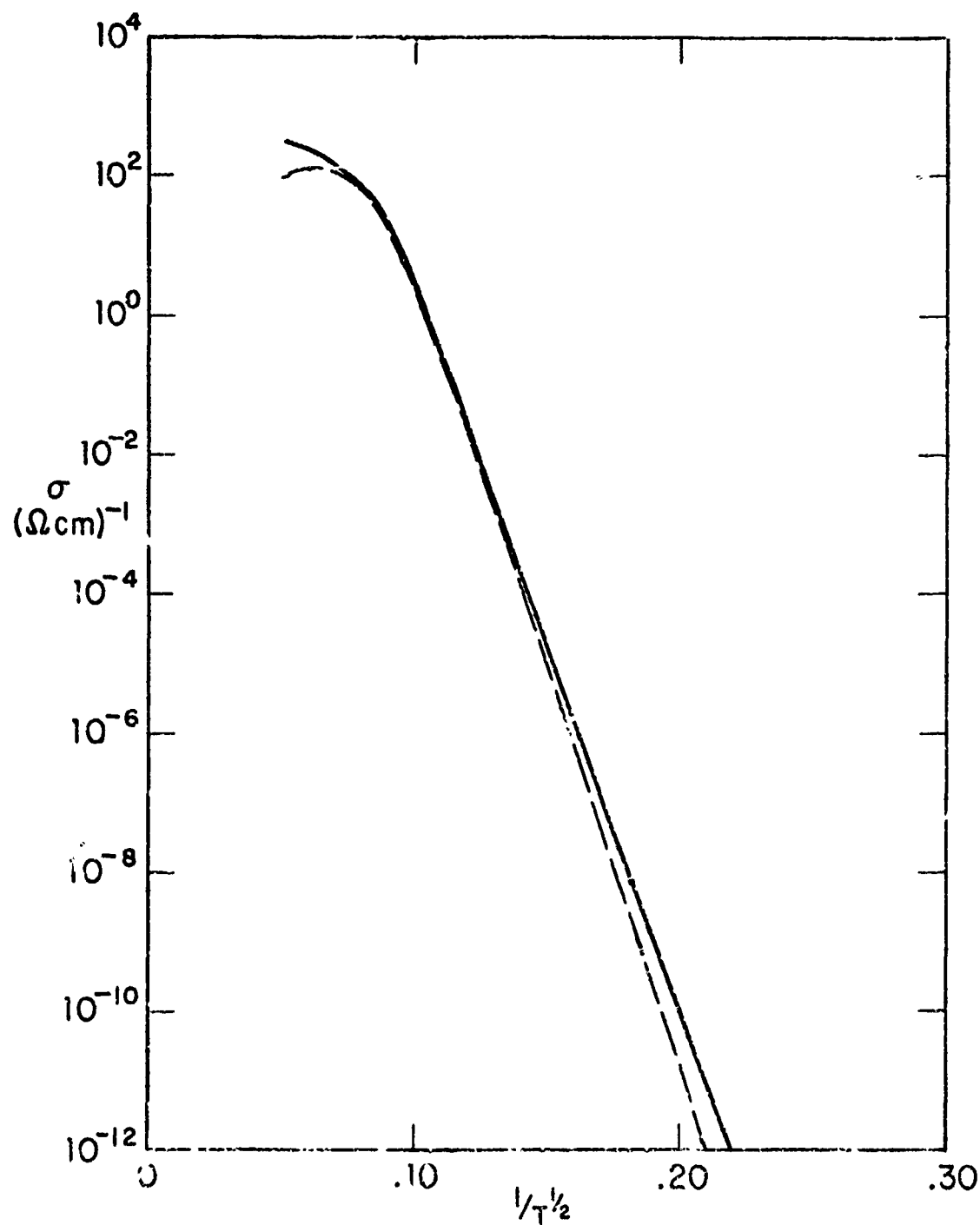


Fig. 1 Plot of conductivity of $K_2Pt(CN)_4Br_{0.3} \cdot nH_2O$ vs. $1/T^{1/2}$.
 Solid Curve: data of Kuse and Zeller, Phys. Rev. Letters 27, 1060 (1971).
 Broken Curve: data of Berenblyum et al., JETP Letters 13, 440 (1971).

Hence one should expect that the conductivity should be describable in terms of a series of hops between the localized states. In collaboration with N. F. Mott we considered the application of this theory to the conductivity of these materials. The essential feature of the model when applied to the one dimensional chains is that it predicts a conductivity, σ whose temperature dependence is given by $\log \sigma \approx T^{-\frac{1}{2}}$. This differs from the three dimensional hopping behavior where $\log \sigma \approx T^{-\frac{1}{4}}$ as has been observed in several amorphous materials such as amorphous Ge (See for example V. Ambegaokar, B. Halperin and J. Langer, Phys. Rev. B 4, 2612 (1971)). As shown in Fig. 1 the conductivity of $K_2Pt(CN)_4Br_{0.3} \cdot nH_2O$ taken from the results of Kuse and Zeller (Phys. Rev. Letters 27, 1060 (1971)) fit the $T^{-\frac{1}{2}}$ temperature dependence very well over a change of nearly fourteen orders of magnitude in the conductivity.

The probability of a hop occurring over a distance R in this model is proportional to

$$\exp \left(-\alpha R - \frac{1}{\rho R k T} \right) \quad (1)$$

where ρ is the density of states per unit length of the chain and α^{-1} is a measure of the localization range. The most probable hopping distance R_{\max} is then obtained by maximizing this expression to obtain:

$$R_{\max} = \left(\frac{1}{\alpha \rho k T} \right)^{\frac{1}{2}} \quad (2)$$

and the conductivity is

$$\sigma = \sigma_0 \exp(-2\alpha R_{\max}) \quad (3)$$

with $\sigma_0 \approx \frac{ne^2 R_{\max}^2 \nu_{ph}}{kT}$ where n is the number of carrier/volume, ν_{ph} a phonon frequency.

Using the optical data of Kuse and Zeller one can estimate that $\rho \approx 0.05$ states/eV-Å and from the T-dependence of Fig. 1, with the use of (2), we find $\alpha^{-1} \approx 16.5\text{Å}$ and R_{max} at $100^\circ\text{K} \approx 200\text{Å}$.

The factor $v_{\text{ph}} \exp(-2\alpha R_{\text{max}})$ in (3) represents the hopping frequency. One would expect on this model that the a.c. conductivity would begin to differ from the d.c. conductivity at frequencies of this order. This behavior has been seen in the ion-radical salts of TCNQ (R. Vlasova, et al. Soviet Physics, Solid State 12, 2979 (1971)) and similar dispersion in the conductivity of $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3} \cdot n\text{H}_2\text{O}$ at 10^{10}Hz (A. Berenblyum et al., JETP Letters 13, 440 (1971)).

The crystals may be considered as built up of regions in which hopping can occur quite readily separated by other regions in which hopping is not easy. This would explain the large dielectric constant observed in these materials as resulting from the polarization of the relatively highly conductive regions. (See A. Berenblyum et al., JETP Letters 13, 440 (1971) and M. Pollak and T. H. Geballe, Phys. Rev. 122, 1742 (1961).)

In an independent piece of work essentially the same conclusion to ours has been reached by A. Bloch, B. Weisman and C. M. Varma. This is about to be published in Physical Review Letters.

The above results have clarified the conductivity mechanism in the Krogmann salts. The weakly localized nature of the states suggest that with a further reduction in the disorder field much more highly conductive materials might be possible. Also the possibility of superconductivity occurring in these materials by the phonon mechanism has been reopened. Further experimental work is required to fix more precisely the parameters of the model and to see whether the random field produced by the ions can account fully for the observed localization range.

Screening in One Dimension - D. Davis

Materials which possess a partially filled conduction band provide a degree of freedom for these electrons or holes which allows them to react to a source charge in such a way as to reduce the magnitude of the potential of this charge. This screening has been dealt with in several ways in the case of three dimensional bulk metals (L. H. Thomas, Proc. Cambridge Phil. Soc. 23, 542 (1927); E. Fermi, Z. Physik 48, 73 (1928); J. Friedel, Phil. Mag. 43, 153 (1952), Nuovo Cimento 7, 287 suppl. 2 (1958); J. S. Langer and S. H. Vosko, J. Phys. Chem. Solids 12, 196 (1959)). A particularly appealing method for solving the problem is the use of the Thomas-Fermi approximation. This approach takes advantage of the simple relationship between the local density of electrons and the corresponding local potential for an electron gas which is in the lowest quantum state and for which the electron density is large in regions sufficiently small that the change in the potential energy is small compared with the mean total energy of an electron (N. F. Mott and H. Jones, The Theory of the Properties of Metals and Alloys, Dover, New York (1958) p. 48).

$$n(r) = \frac{-e}{3\pi^2} \left\{ \frac{2m}{\hbar^2} (E_f + e\phi) \right\}^{3/2} \quad (1)$$

Combining this with Poisson's equation gives a differential equation for the electrostatic potential,

$$\nabla^2 \phi = \kappa^2 \phi \quad (2)$$

where $\kappa = 2 \left(\frac{3n_0}{\pi a_0^3} \right)^{1/6}$ is the reciprocal of the screening length, l_s .

Applying this relationship to the case of a source charge at the origin in a bulk material with overall electron density n_0 gives a screened potential

of the form

$$\Phi(r) = \frac{1}{r} e^{-\kappa r}$$

The solution for three dimensions shows that a great deal of screening occurs and the question arises as to whether or not such screening is possible if the freedom of the electrons is restricted by confining their motion to particular regions in space. Kuper (Phys. Rev. 150, 189 (1966)) proposed that any such restriction would be unable to reduce the static screening length. Indeed this appears to be the case, but his further conclusion as to the magnitude of the increase for electrons confined to a filament is inconclusive since it ignores the presence of neighboring filaments in actual compounds. By enlarging upon Kuper's model we have been able to take into account the presence of the surrounding material on the central filament.

Model

We have obtained numerical solutions to the enlarged model which considers screening to occur in two regions of space, Fig. 1. The central filament of radius R_1 represents metal atoms and κ for this region is determined by the density of electrons in the bulk metal. Surrounding the filament is a coaxial cylinder extending from an inner radius R_2 to infinity. For this region κ' is determined by the density of conduction electrons in the particular material of interest. Generally $\kappa' < \kappa$ since n_0 will be smaller in compounds of a metal than in the pure metal itself.

Results

We chose to describe the compound $K_2Pt(CN)_4Cl_{0.32} \cdot 2.6H_2O$ in which the Pt atoms have a formal oxidation state +2.32. The lattice constants

(K. Krogmann, Angew. Chem., Int. ed. 8, 35 (1969)) are $a = b = 9.87$ and $c = 2.89 \text{ \AA}$ giving a density of holes for the bulk material of 1.14×10^{21} holes/cm³, and $\kappa' = 0.88 \text{ \AA}^{-1}$. The value for κ for the filament was obtained by multiplying the density of conduction electrons in metallic platinum by 0.32 giving 21.2×10^{21} electrons/cm³ and $\kappa = 1.44 \text{ \AA}^{-1}$.

Calculations were performed for both Kuper's model* and the enlarged model. Fig. 2 shows a comparison of the results. Although little screening occurs in the case of a single filament for the region between R_1 and R_2 , the addition of the outer cylinder substantially reduced the potential in this intermediate region. As expected the screening was not total as shown by the position of the fully screened potential using the value κ' . Calculations were performed for values of z other than zero. A "least squares fit" to a function of the form of Eqn. (3) gave an effective value of $\kappa_{\text{eff}} = 0.15$. The potential was found to be largely isotropic.

Conclusions

Screening in materials which are characteristically one dimensional cannot be described simply by results obtained from models which ignore the three dimensional nature of the bulk material. Instead the screening is intermediate between the cases of a single filament and bulk screening. However, the close relationship to bulk screening is shown by the isotropic form of the screened potential, as has been observed by Visscher and Falicov in the case of two dimensional screening (Phys. Rev. B2, 2541 (1971)).

* Expressions used in the solution of this model were rederived eliminating several errors which appeared in the publication.

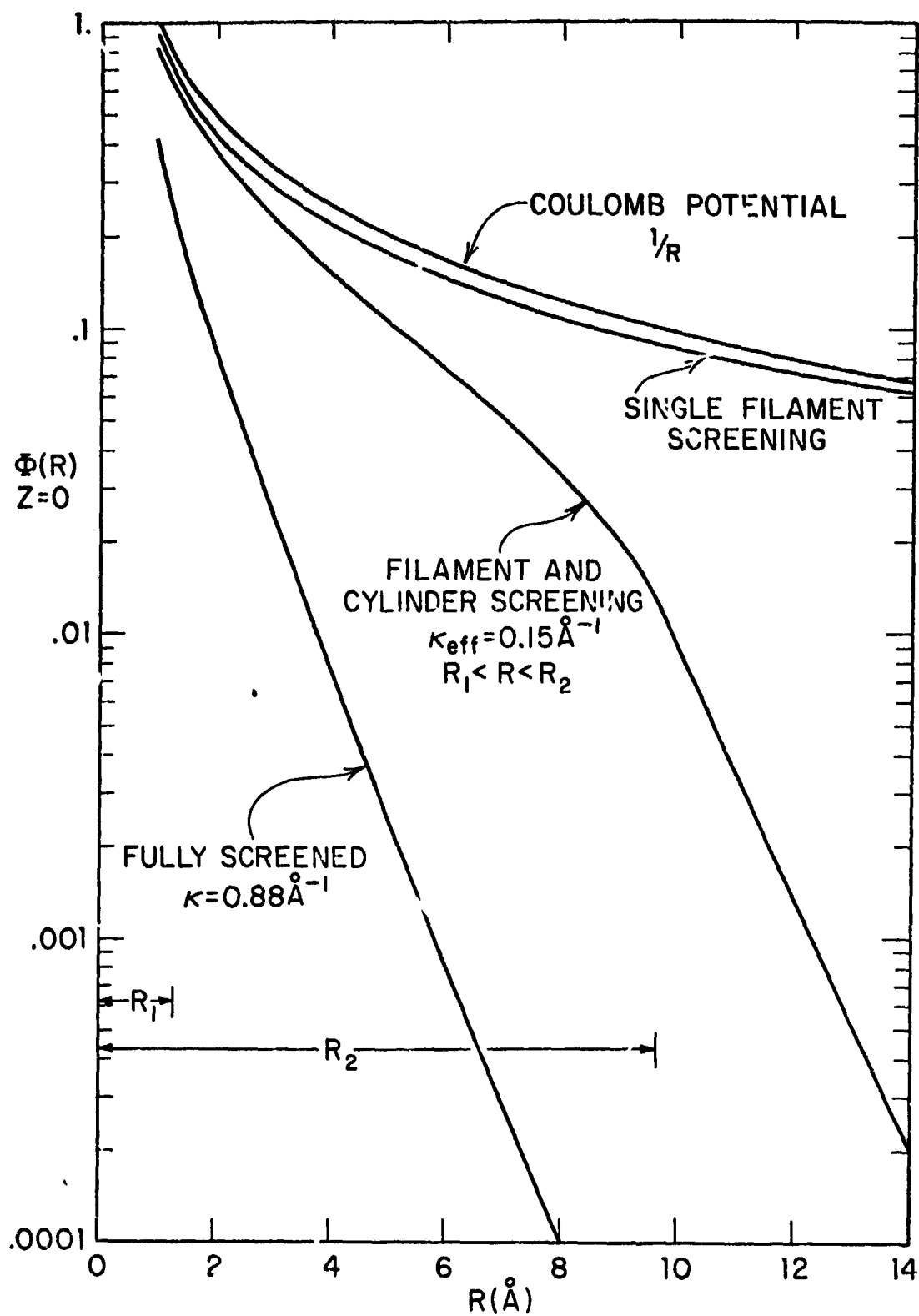


Fig. 2 Potential due to unit source charge

A further conclusion drawn by Kuper that the screening in one dimension is insufficient to reduce the Coulomb potential to a point where it can be dominated by an attractive excitonic interaction as suggested by Little is likewise unsupportable in view of these results. Indeed, Dzyaloshinskii and Katz (Soviet Physics JETP 28, 173 (1969)), treating the case of an array of parallel filaments, conclude that superconductivity is possible for their model.

Screening in Concentric Shell Structures - B. Bush

A FORTRAN program, "AXIAL", has been written and tested to compute dielectric screening by an electron gas which is uniform in one dimension (z) but constrained in concentric shells in the lateral (xy) plane. This model is meant to apply to crystals in which electrons delocalize along parallel filaments composed of stacked square-planar metal complexes. The innermost zone of the model represents one filament; the surrounding zones represent the averaged effect of first-, second-, ... nearest neighbor filaments, separated by shells of interstitial material - for example, organic dyes.

Since the dielectric response function is computed in terms of z-momentum and frequency ω , results are directly applicable to calculation of ω -dependent matrix elements between conduction-electron states on the filaments, and also between these electrons and molecular excitons on the dyes. The program accommodates any desired dimensions for the filament lattice, electron density of states, and ω -dependent dye polarizabilities in the longitudinal and radial directions.

Although the screening calculation is equally easy using three- or one-dimensional RPA response functions, for many physically interesting systems the typical longitudinal electron spacing is neither much greater than lateral filament dimensions (one-dimensional electron gas) nor much less (three-dimensional regime). In the intermediate case, screening lengths are comparable with filament radii, and several transverse states of the filament are excited by the self-consistent potential.

The resultant non-local "surface effects" are now being computed using transverse harmonic oscillator states (much as was done for semi-infinite geometry by D. News, Phys. Rev. B₁, 330⁴ (1970)). With luck, the partially

three-dimensional gas will simply display intermediate values of the RPA function which plugs into the AXIAL calculation. If, however, the non-local character of the transverse response predominates (as in the semi-infinite case) a somewhat greater modification of AXIAL will be needed.

Band Theory - A. Abarbanel

Work has continued on the band theory phase of the calculations as proposed in the previous report. The Green's function method is now fully programmed for handling the type of structures whose syntheses are being carried out. The programs are capable of calculating both wave functions and energy levels for electrons in the one-dimensional periodic arrays.

Actual structures are now being studied in a two step procedure. The first step involves calculation of electron states in the isolated unit cell. This part can then be checked against both experimental and theoretical work carried out earlier by other workers. Comparing the present computations with other approaches contributes a good deal of insight into this as well as the other methods

The second step involves handling the entire one-dimensional periodic structure. Except that the use of Bloch symmetry in handling the entire lattice is involved, the two steps of the calculation are somewhat similar in form. This is advantageous, because it allows one to see directly the changes in electron structure that result in the change from one unit cell to an array of unit cells.

Present work is centering on the above considerations, as well as refinements in the calculations to relax whichever initial approximation may prove too restrictive.

III. SYNTHETIC PROGRAM

Introduction:

Efforts are continuing in three major directions: preparation of linear covalent trimetallic monomers; introduction of dye substituents into ligands which are associated with intra crystalline metallic chains; and the synthesis of molecular mixed valence, "Krogmann" complexes which possess an organic ligand which is capable of further elaboration. As outlined in the following sections, progress has been made in each of these areas.

Murphy has been able to prepare the Sn-Rh-Sn trimer using the rhodium(I) - DOh complex. Hoyano and Stark have prepared and characterized the first tin hydrides which have a transition metal bonded to tin and experiments have begun which are designed to develop the tin-tin coupling reaction we intend to use in the intermetallic polymer synthesis.

Libit has prepared the first azulene substituted β -diketones as well as other chelating ligands which have long hydrocarbon side chains. It is now clear that the stacking of planar d^8 systems, which gives rise to metal-metal interactions, is the result of fortuitous van der Waal's interactions and will be disrupted by small structural perturbations. MacLaury continues to explore methods of preparing and characterizing molecular mixed valence complexes of the type described earlier by Joan Valentine (cf. last six month technical report).

Semi-Annual Research Report

Don Murphy

February, 1972

Work on the synthesis of linear intermetallic monomers suitable for polymerization has continued. Previously linear monomer systems were based on the cobalt bis(diacetylmonoximeimino)propane (DOH)¹ and osmium tetracarbonyl² systems. While both of these systems gave the desired trans configuration of organotin moieties necessary to avoid cyclization, the cobalt compounds suffered from a reactive cobalt-tin bond which prevented subsequent functionalization of the tin, and the osmium system, which could be functionalized, suffers from cis trans isomerization problems upon making tin hydrides in the final step before polymerization.

In an attempt to combine the stability of the osmium compounds with the fixed stereochemistry of the cobalt system, synthesis of compounds in the previously unstudied rhodium (DOH) system was undertaken. All compounds reported¹ in the cobalt series have been prepared now with rhodium, but as yet the reactivity of the rhodium tin bond has prevented functionalization.

Although the same compounds can be prepared in both Co and Rh DOH systems, the synthetic route is quite different. Synthesis of

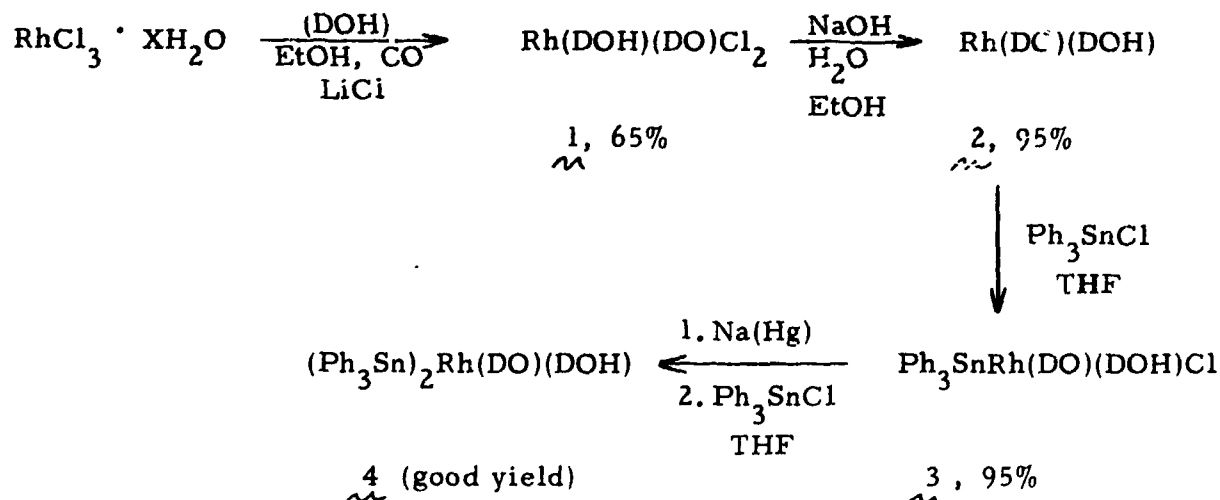
$\text{Rh}(\text{DO})(\text{DOH})\text{Cl}_2$, 1, was first accomplished in our laboratory by Mr. R. Gagne, and has been refined to give a good yield (65%) of the starting complex by treating $\text{RhCl}_3 \cdot x \text{H}_2\text{O}$ with (DCH) in ethanol in the presence of CO and excess chloride. The reaction involves either a catalytic amount of labile $\text{Rh}(\text{I})^3$ or a reactive $\text{Rh}(\text{III})$ hydride⁴ and has been used to prepare other tetrasubstituted nitrogenous complexes of $\text{Rh}(\text{III})^3, 4$

The preparation of bis tin complexes of cobalt (DOH) were (1) treatment of $\text{Co}(\text{DO})(\text{DOH})\text{I}_2$ with R_3SnLi and (2) treating $\text{Co}(\text{DO})(\text{DOH})\text{I}_2$ and R_3SnCl with NaBH_4 . Reaction type (1) does not go with rhodium and in (2) R_3SnCl is reduced faster than $\text{Rh}(\text{DO})(\text{DOH})\text{Cl}_2$ and gives a product identical to that obtained by treating 1 with R_3SnH , which appears to contain one R_3Sn unit and one chloride per rhodium in a structure wherein the oxime bridge has been broken.

Alternatively, it has been found that, unlike the cobalt complex, the square $\text{Rh}(\text{I})$ complex $\text{Rh}(\text{DO})(\text{DOH})$, 2, may be prepared in high yield by treating 1 with basic aqueous ethanol. The $\text{Rh}(\text{I})$ complex forms as tiny green-gold crystals with a metallic luster suggestive of metal-metal interaction in the solid common for square planar complexes of Rh, Ir, and Pt. The compound has proven too insoluble to grow larger crystals.

The $\text{Rh}(\text{I})$ complex adds one mole of Ph_3SnCl nearly quantitatively to give $\text{Ph}_3\text{Sn}-\text{Rh}(\text{DO})(\text{DOH})\text{Cl}$, 3. The chloride in 3 appears to be somewhat labile as suggested by an apparent ionization of the complex in warm ethanol, although no product has been isolated.

Treatment of 3 with sodium amalgam, followed by Ph_3SnCl gives the desired di-substituted tin derivative $(\text{Ph}_3\text{Sn})_2\text{Rh}(\text{DO})(\text{DOH})$, 4. The synthetic route to this complex in summary is



The last step has not been performed for yield, but it appears to be quite good so that a reasonable yield route to di-substituted tin complexes is now available. Alkyl tin chlorides add readily to the square $\text{Rh}(\text{I})$ derivative. The bis alkyl tin derivatives however, are quite air sensitive and have not been isolated in pure form to date.

The $\text{Rh}(\text{DOH})(\text{DO})$ unit is too large to accommodate two rhodiums about one tin. This is evident from space filling models and is confirmed by experimentation. Thus, Ph_2SnCl_2 gives only $\text{ClPh}_2\text{SnRh}(\text{DO})(\text{DOH})\text{Cl}$.

Electrophilic reactions aimed at functionalizing the tins, lead instead to cleavage of the Rh-Sn bonds.

For the moment work on this system is stymied because of our failure to impose the proper functionality on the tins. One possibility is

to first make the bis SnCl_3 derivative and attempt to use Grignard reactions to build up to the desired diorganohalo derivative. Work on this and related reactions is continuing.

Experimental

1-(diacetylmonoximato-imino)-3-(diacetylmonoxime-imino)propane rhodium dichloride, 1

To an ethanol solution (200 ml) containing 2.5g LiCl purged with a CO bubble, 2.5g solid $\text{RhCl}_3 \cdot \text{X H}_2\text{O}$ (47% Rh) and 4.0g (DOH) were added successively. The mixture was stirred for 0.5 hours and refluxed for four hours while maintaining the CO bubble. After cooling the mixture was filtered and the solid extracted with CH_2Cl_2 and crystallized by addition of ethanol. Yield = 2.4g = 60%. Anal. Calculated for $\text{C}_{11}\text{H}_{19}\text{N}_4\text{O}_2\text{RhCl}_2$: C, 31.96; H, 4.60; N, 13.55; Cl, 17.24. Found: C, 32.00; H, 4.55; N, 13.71; Cl, 17.18.

1-(diacetylmonoximato-imino)-3-(diacetylmonoxime-imino)propane rhodium(I), 2

A stirred slurry of 1 (300 mg = 0.72 mmol) in 2 ml degassed ethanol was treated with 2 ml degassed water containing 150 mg NaOH . The resulting gold green flakes were filtered under inert atmosphere and washed with water, ethanol, and ether. The product is air sensitive even in the solid state. Yield = 230 mg = 92%. Anal. Calculated for $\text{C}_{11}\text{H}_{19}\text{N}_4\text{O}_2\text{Rh}$: C, 38.61; H, 5.60; N, 16.37; Cl, 0.00. Found: C, 38.45; H, 5.66; N, 16.88; Cl, 0.00.

triphenyltin 1-(diacetylmonoximato-imino)-3-(diacetylmonoxime-imino)
propane rhodium chloride, 3

A slurry of 2 (100 mg = 0.29 mmol) in THF (5 ml) was treated with Ph_3SnCl (150 mg = 0.39 mmol) in THF (5 ml) and stirred for two hours. The mixture was filtered and the solid extracted with CH_2Cl_2 and crystallized with hexane. Yield = 210 mg = 99%. Calculated for $\text{C}_{29}\text{H}_{34}\text{N}_4\text{O}_2\text{RhSnCl}$: C, 47.86; H, 4.70; N, 7.71; Cl, 4.87. Found: C, 47.43; H, 4.67; N, 7.94; Cl, 5.28.

bis(triphenyltin)-1-(diacetylmonoximato-imino)-3-(diacetylmonoximeimino)
propane rhodium

A solution of 3 (100 mg = 0.14 mmol) in 5 ml THF was treated with excess Na(Hg) for two hours to give a blue solution. After removal of the Na(Hg) , Ph_3SnCl (150 mg = 0.39 mmol) was added and stirred ten minutes. The solution was filtered and crystallized under inert atmosphere to give the orange product. Recrystallized from CH_2Cl_2 - Et_2O . Calculated for $\text{C}_{47}\text{H}_{49}\text{N}_4\text{O}_2\text{Sn}_2\text{Rh}$: C, 54.16; H, 4.72; N, 5.37. Found: C, 53.36; H, 4.75; N, 5.47.

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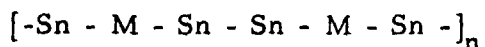
Semi-Annual Research Report

James K. Hoyano

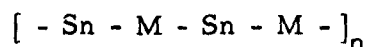
February, 1972

Introduction

Previous research reports from this group have outlined some approaches and results towards the synthesis of linear molecular polymers with backbones comprised entirely of covalently bonded metal atoms.¹ Some of the more promising linear polymers appear to be ones which contain low-valent transition metals either directly in the polymeric backbone or appended to a chain of tin or germanium atoms. Some possibilities are shown below for tin, at present the most suitable main group metal.

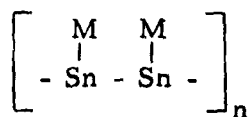


(a)

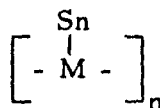


(b)

M = transition metal
moiety including any
ancillary ligands



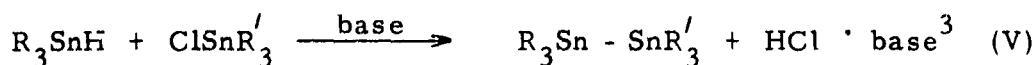
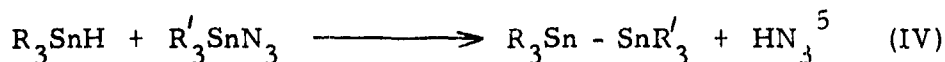
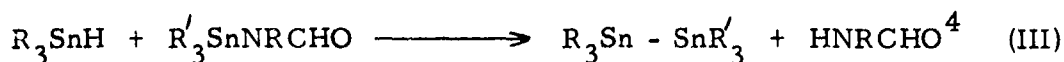
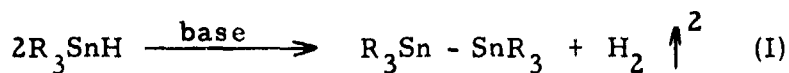
(c)



(d)

Of the above, progress towards the synthesis of polymers of type (a) are at the most advanced stage. Potential monomers containing metal atoms in the required linear array (Sn-M-Sn) have been synthesized by D. Murphy. With the tin atoms properly functionalized, the monomer may be made to polymerize to form the required linear polymer.

Work by Murphy led to the synthesis of the first known stable (transition metal) tin hydride $(CO)_5Mn-SnH(C_6H_5)_2$, which is a suitable model compound for studying the tin-tin coupling reaction. The tin-hydride function has been reported as an effective means for tin-tin bond formation.



If one of the above coupling reactions can be applied to selectively couple (transition-metal) tin hydrides such as $Ph_2HSnMn(CO)_5$, the eventual application to an appropriate linear system (-Sn-M-Sn-) would lead to the desired polymer. Work on simple monomeric systems may shed more light on tin-tin bonded systems which contain appended transition metals. Very little is known about these systems and in fact the Sn-Sn bonds may be enhanced when transition metals are present.

This report describes the synthesis and properties of some new (transition-metal) tin hydrides. Preliminary Sn-Sn coupling attempts of these hydrides and related experiments are also described.

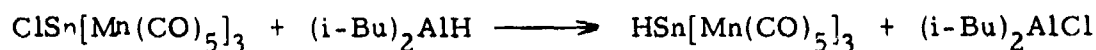
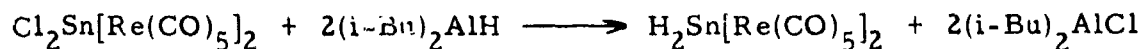
Results and Discussion

A. (Transition-metal)tin hydrides

The successful use of diisobutylaluminum hydride (in hydrocarbon solvents) in reducing (transition-metal)tin chlorides to the corresponding hydrides has been described by D. Murphy.¹ This technique has now been applied to a variety of other (transition-metal)tin chlorides and in some cases stable hydrides were isolated.

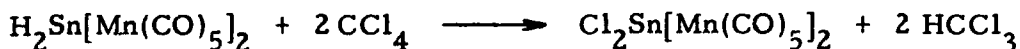
The starting (transition-metal)tin chlorides used in the reductions were prepared according to published procedures with slight modifications in some cases; preparative methods and appropriate references are given in the Experimental Section.

The reductions were carried out in hydrocarbon solvents using a slight excess of the reducing agent (i-Bu)₂AlH. The following scheme summarizes the successful reactions where the expected hydrides were isolated.



These three hydrides are moderately air-stable crystalline solids ranging in color from pale-yellow to orange. Characterization by infrared and nmr spectroscopy and elemental analyses were consistent with the

expected formulations. Similar to simple organotin hydrides these (transition metal)tin hydrides reacted with carbon tetrachloride exothermically to form the chloride and chloroform.



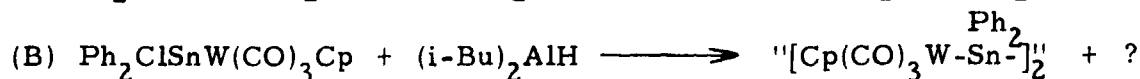
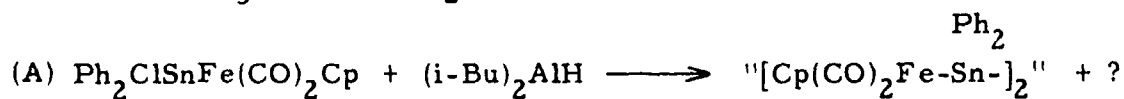
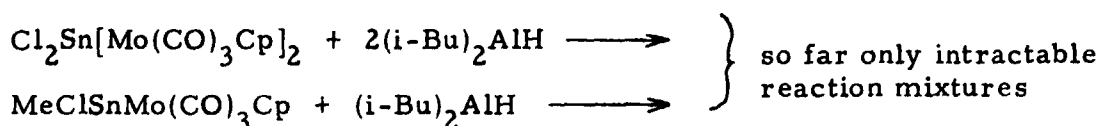
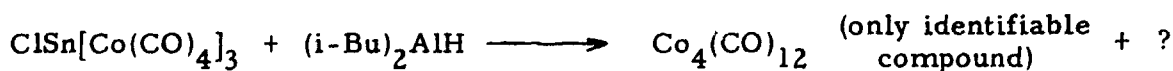
As mentioned previously, these are the only known cases so far (along with $\text{Ph}_2\text{HSnMn}(\text{CO})_5$ prepared by Murphy) of tin hydrides coordinated to transition metals. It is interesting that only compounds with manganese and its third row congener rhenium as the transition metal have been isolated; it appears that the stability of this type of hydride is dependent on the type of transition metal moiety appended as indicated by the unsuccessful reductions described below. However, the number of transition metals bonded to the tin atom does not appear to affect the stability of the hydride. Qualitatively the compound $\text{HSn}[\text{Mn}(\text{CO})_5]_3$ appears to be the most stable.

A few stable germanium analogs such as $\text{H}_2\text{Ge}[\text{Mn}(\text{CO})_5]_2$ ⁶ and $\text{H}_2\text{Ge}[\text{Fe}(\text{CO})_2\text{Cp}]_2$ ⁷ are known and appear to be more stable than the tin compounds. The isolation of $\text{H}_2\text{Sn}[\text{Fe}(\text{CO})_2\text{Cp}]_2$ has been attempted by Wilkinson⁸ and by N. Nelson¹ in this laboratory but the hydride could not be isolated. Numerous stable transition metal-silicon hydrides such as $\text{Ph}_2\text{HSiFe}(\text{CO})_2\text{Cp}$,⁹ $\text{Ph}_2\text{HSiMn}(\text{CO})_5$,⁹ $\text{H}_3\text{SiMn}(\text{CO})_5$,¹⁰ $\text{H}_3\text{SiCo}(\text{CO})_4$,¹¹ and $(\text{H}_3\text{Si})_2\text{Fe}(\text{CO})_4$ ¹² are known. Thus, it appears that the general order of stability of the (transition metal)-metal hydrides is $\text{Si} > \text{Ge} > \text{Sn}$.

There appears to be no reason why the as yet unreported compounds such as $\text{HGe}[\text{Mn}(\text{CO})_5]_3$, and $\text{H}_2\text{Ge}[\text{Re}(\text{CO})_5]_2$ cannot be prepared by reducing their corresponding chlorides with diisobutylaluminum hydride.

The above illustrates why the tin or germanium hydrides are the most suitable for investigations on the eventual linear polymer formation. The silicon hydrides appear to be too unreactive for subsequent silicon-silicon bond forming reactions.

Reductions were attempted on various other (transition-metal)tin chlorides and the results (or the lack thereof) are shown below.

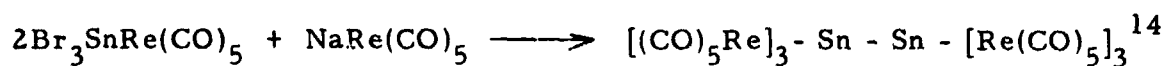
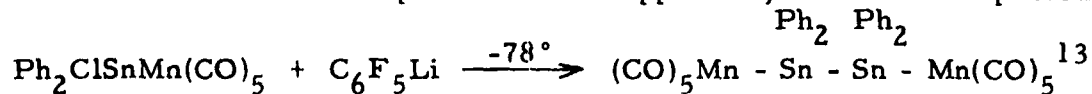


In all cases some type of reaction occurred but in most instances many products were formed (by TLC) making separation of individual components very difficult. However, it did appear that initially the required hydrides were formed and subsequently decomposed because of their presumed instability. For the case of the cobalt compound $\text{ClSn}[\text{Co}(\text{CO})_4]_3$, it appeared that even the (transition-metal)tin bonds were cleaved to some extent. The last two reactions (equations (A) and (B) appear to be the most promising with regard to revealing the fate of these apparently instable hydrides. Some evidence (infrared and nmr) has been obtained that indicates that the decomposition leads to the coupled products as shown. Efforts so far have failed to afford these compounds in the pure

form. Some work will be continued in the above vein but some related and more promising approaches toward the study of tin-tin coupled compounds containing coordinated transition metals will now be described.

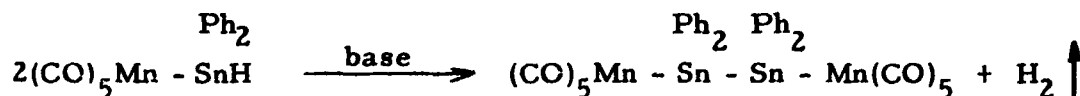
B. Tin-tin bonded compounds containing coordinated transition metals.

Although numerous compounds containing covalently bonded tin atoms are known, only two cases can be found in the literature where covalent tin-tin and (transition-metal)tin bonds are present in the same molecule. Even for these cases the products were apparently obtained unexpectedly.



Beginning with (transition-metal)tin compounds one can attempt to systematically synthesize tin-tin compounds containing coordinated transition metals by applying reactions which have been reported to be effective for coupling simple organotin compounds. Most of these reactions (neglecting ionic reactions which would be unsuited for the ultimate polymer formation) involve the use of tin hydrides in one form or another. A general picture of these coupling reactions was given in the introduction (see equations I to VI). A preliminary probe of these reactions applied to some of the available (transition-metal)tin compounds will now be given.

Applying the hydrogen elimination reaction to a (transition-metal)tin hydride, one would expect the coupled product, e. g.

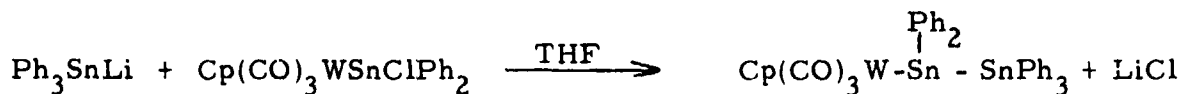


The coupled product for this case is a known compound¹³ and comparison with the known physical properties simplifies characterization of the product. This system is currently under investigation by R. Stark.¹⁵

The hydrogen elimination reaction when applied to the dihydrides $\text{H}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$ and $\text{H}_2\text{Sn}[\text{Re}(\text{CO})_5]_2$ using various bases and concentrations (pyridine, Et_3N , $i\text{-BuNH}_2$) has so far given inseparable mixtures of sparingly soluble compounds. These compounds are probably cyclic tin systems of various sizes. The coupling of these dihydrides will be deferred until simpler monohydride systems are understood more fully.

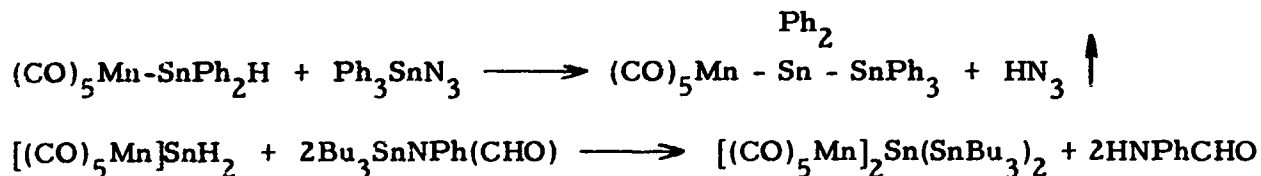
The monohydride $\text{HSn}[\text{Mn}(\text{CO})_5]_3$ was very unreactive to the hydrogen elimination reaction conditions and forcing conditions led to decomposition. It may be that the coupled product does not form readily due to steric problems.

At this point some attempt was made to attach an organotin group to a (transition-metal)tin compound via organotin lithium salts.

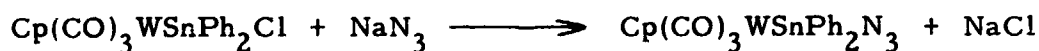


However, attempts with $\text{Ph}_2\text{ClSnMn}(\text{CO})_5$, $\text{Ph}_2\text{ClSnFe}(\text{CO})_2\text{Cp}$, and $\text{Ph}_2\text{ClSnW}(\text{CO})_3\text{Cp}$ resulted mainly in the formation of $\text{Ph}_3\text{Sn-SnPh}_3$ and recovered (transition metal)tin chloride.

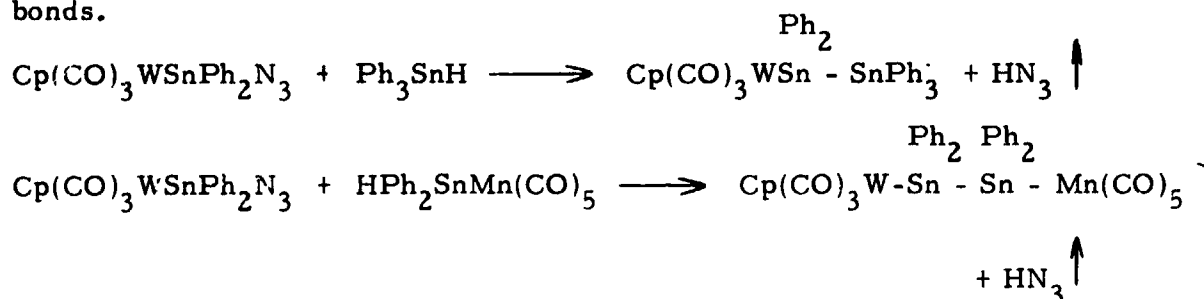
Various tin-nitrogen species react with tin hydrides to form tin-tin bonds (equations II-IV). In this regard the compounds Ph_3SnN_3 ¹⁶ and $\text{Bu}_3\text{SnNPh(CHO)}$ ¹⁷ have been prepared and attempts are being made to find the optimum conditions for coupling:



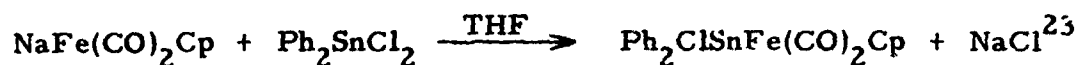
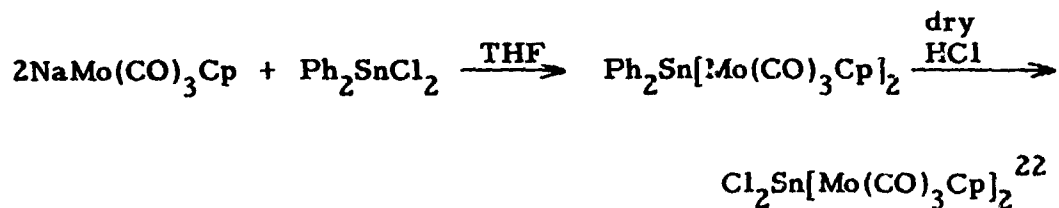
A possible variation of the above type of reaction may be used because of the recent preparation of a stable crystalline (transition metal)tin azide.



The preparation of this azide suggests some reactions for forming tin-tin bonds.



Undoubtedly other (transition metal)tin-azides and -amides can be prepared. Reaction of these tin-nitrogen compounds not only with tin hydrides but possibly with some suitable transition metal hydrides¹⁸ may suggest an appropriate approach to linear polymers containing alternating transition metal and tin atoms.



The compound $\text{Ph}_2\text{ClSnW}(\text{CO})_3\text{Cp}$ has not been previously reported; it was prepared analogously to that given above for $\text{Me}_2\text{ClSnMo}(\text{CO})_3\text{Cp}$. Tungsten hexacarbonyl (6.50g, 18.5 mmol) was added to a solution of NaC_5H_5 (20 mmol) in 30 ml diglyme and heated to 170-175° for five hours until CO evolution ceased. After cooling the brown solution of $\text{Cp}(\text{CO})_3\text{WNa}$ to room temperature, Ph_2SnCl_2 (6.40 g, 18.6 mmol) was added at once and the mixture was stirred at room temperature overnight. The resulting dark mixture was filtered; water was then added to the filtrate to induce precipitation of the product. After filtration and drying, the crude product was chromatographed on a silica gel column (chloroform elution). The main band was collected and recrystallized from chloroform-hexane to afford pale-yellow crystals (5.0 g, 45%) of the product: mp 167-169°; nmr spectrum (CDCl_3) τ 2.50 (complex multiplet 10 H), τ 4.52 (singlet 5H); ir (CHCl_3) 2018s, 1948ms, 1913s cm^{-1} . Anal. Calcd for $\text{C}_{20}\text{H}_{15}\text{O}_3\text{ClWSn}$: C, 37.45; H, 2.36. Found: C, 37.23; H, 2.35.

Dihydridobis(pentacarbonylmanganese)tin (IV), $H_2Sn[Mn(CO)_5]_2$.

A stirred suspension of $Cl_2Sn[Mn(CO)_5]_2$ (0.90g, 1.55 mmol) in 10 ml hexane was treated with diisobutylaluminum hydride (3.2 mmol in heptane solution). After fifteen minutes a clear orange solution formed. The solution was concentrated to ca half volume and cooled to -20° . The orange precipitate was crystallized twice from hexane to afford pale-yellow crystals of the product (0.60 g, 75%): mp $89-91^\circ$ (with decomposition); nmr spectrum (C_6D_6) τ 6.10 (sharp singlet); ir (hexane) $1770m$ (ν Sn-H), $2105w$, $2080ms$, $2010s$, $1995s$, $1975m$ cm^{-1} . Anal. Calcd for $C_{10}H_2O_{10}Mn_2Sn$: C, 23.50; H, 0.50. Found: C, 23.43; H, 0.71.

The compound dihydridobis(pentacarbonylrhenium)tin (IV), $H_2Sn[Re(CO)_5]_2$, was prepared in an analogous manner to the above to afford a yellow crystalline product in 80% yield: mp $94-97^\circ$; nmr spectrum (toluene) τ 6.35 (sharp singlet); ir (hexane) 1760 (ν Sn-H), $2105ms$, $2023s$, $2005m$, $1995s$, $1975m$ cm^{-1} . Anal. Calcd for $C_{10}H_2O_{10}Re_2Sn$: C, 15.55; H, 0.26. Found: C, 15.85; H, 0.39.

Hydridotris(pentacarbonylmanganese)tin (IV), $HSn[Mn(CO)_5]_3$.

A solution of $ClSn[Mn(CO)_5]_3$ (0.74 g, 1.0 mmol) in 15 ml toluene was treated with diisobutylaluminum hydride (1.5 mmol in heptane solution). The solution was stirred at room temperature for two hours and then cooled at -20° to induce crystallization. The crude product was recrystallized from toluene to afford orange crystals (0.50 g, 70%) of

product: mp 127-130° (with decomposition); nmr (CD_2Cl_2) τ 6.50 (sharp singlet); ir (CH_2Cl_2) 1730m ($\nu_{\text{Sn-H}}$), 2075ms, 2030m, 2005s, 1995s, 1970m cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{HO}_{15}\text{Mn}_3\text{Sn}$, C, 25.57; H, 0.14. Found: C, 25.51; H, 0.32.

Diphenylazidotin(π -cyclopentadienyl)tricarbonyltungsten, $\text{Cp}(\text{CO})_3\text{WSnPh}_2\text{N}_3$.

A solution of $\text{Cp}(\text{CO})_3\text{WSnClPh}_2$ (1.60 g, 2.5 mmol) in 125 ml diethylether and a solution of NaN_3 (0.25 g, 3.8 mmol) in 50 ml distilled water were shaken together for 10 minutes in a 500 ml separatory funnel. Separation of the ether layer, drying over sodium sulfate and evaporation gave a white solid. This solid was recrystallized twice from hexane-chloroform to afford white crystals of the product (1.3 g, 80%); mp 145-148°; nmr (CDCl_3) τ 2.55 (aromatic multiplet 10H), τ 4.40 (singlet 5H); ir (CDCl_3) 2075s (ν_{azide}), 2000s, 1937s, 1905s cm^{-1} . Anal. Calcd for: $\text{C}_{20}\text{H}_{15}\text{O}_3\text{WSnN}_3$; C, 37.04; H, 2.32; N, 6.48. Found: C, 37.27; H, 2.46; N, 6.05.

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Hydridotin Transition Metal Complexes

Semi-Annual Research Report

by

Rex Stark

November, 1971

Since the time of my last report,¹ my research activities have been concentrated in two areas. Considerable time was spent in attempts to expand and improve on the work of Dr. Manning Cooke,¹ and in particular to synthesize dodecamethylcyclohexagermane in high yield. This synthesis was not successful. Because this extremely important synthesis could not be worked out to my satisfaction, and because of other difficulties in the studies of Ge-Ge coupling,² the germanium problem has been deferred. Current research concerns the more urgent (and more tractable) problem of synthesizing tin polymers containing transition metal units. Our current approach to these polymers is by way of tin hydrides bonded to transition metals. This previously unknown class of compounds is expected to have great utility in the synthesis of potentially superconducting materials. Dr. Hoyano and I will be preparing a series of these hydrides and studying their chemical behaviour.

Synthesis of Dodecamethylcyclohexagermane

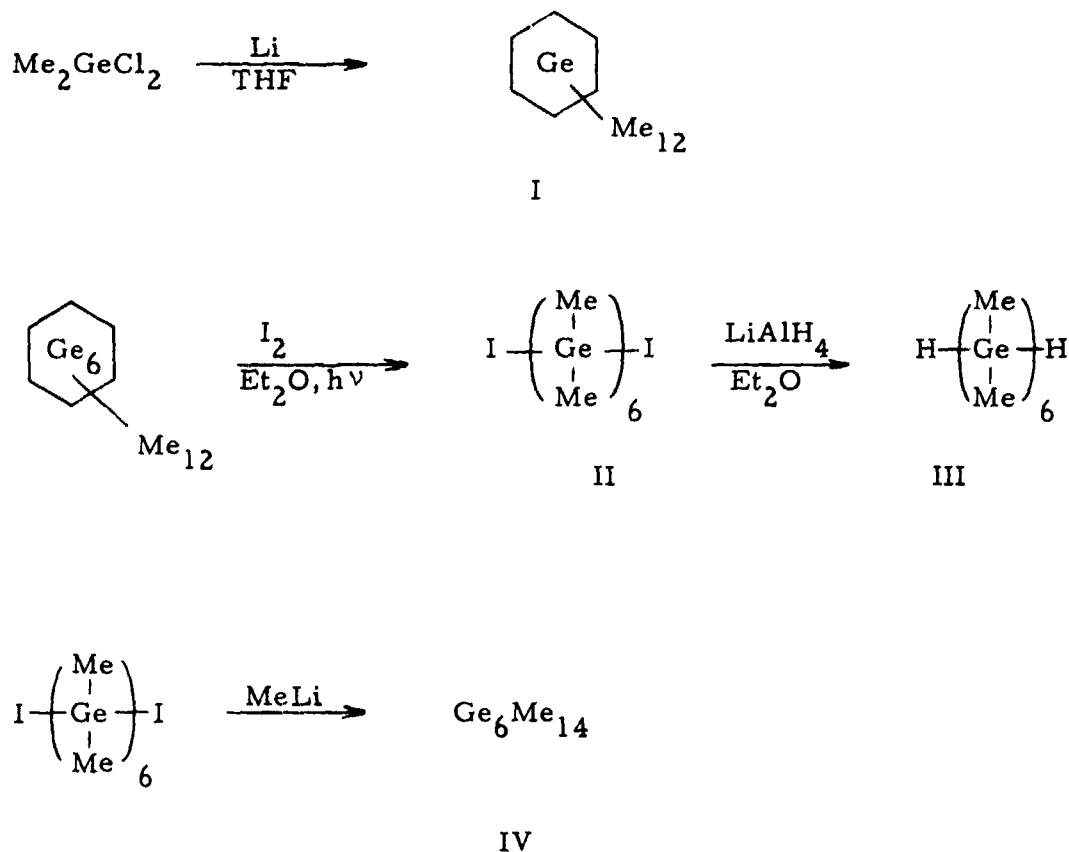
The synthesis of dodecamethylcyclohexagermane from the reaction of dimethylgermanium dichloride with lithium in THF was originally reported by Russian workers,³ who observed formation of the cyclic

hexamer (mp 211° - 213° C) in yields up to 80%. Neither Dr. Cooke nor I have been able to reproduce this synthesis after repeated attempts. Dr. Cooke developed another synthesis in our laboratory,¹ and was able to prepare small amounts of $\text{Ge}_6\text{Me}_{12}$ in yields up to 24%. I have been unable to reproduce Dr. Cooke's work, and in numerous attempts was only once able to isolate a satisfactorily pure product. This attempt involved the use of lithium metal with 1% sodium, and the product was separated from several other components (apparently chlorogermanes) by crystallization. The Russian procedure always resulted in a large number of products in the vpc, with a number of these being collected and studied.

It is difficult to resolve the Russian results with those of our laboratory. It was reported that the reaction took place at 40 - 46°C in THF after a couple of hours. The reaction mixture was diluted, filtered and stripped to give a white crystalline mass "consisting chiefly of $\text{Ge}_6\text{Me}_{12}$ ".³ After 4 - 5 recrystallizations from ethanol, the melting point was 211° - 213° C.

The material made by Dr. Cooke and myself has been passed through the gas chromatograph and found to have a retention time of 2 - 4 minutes (different columns) at 225°C . I consider this unlikely for a material melting at 212°C . The melting behaviour of our material was most unusual in that it melted over an extremely wide range from $\sim 125^{\circ}$ - 200°C , although appearing pure on the vpc (5 - 6 other components present in only small traces). In addition the solid material appears moist, indicating it may be hygroscopic or unstable over long periods of time. Our product is granular, whereas the Russian material was needlelike.

These results suggest that the material prepared in our lab was not $\text{Ge}_6\text{Me}_{12}$, but work by Dr. Cooke¹ confirms the identity of the product. The $\text{Ge}_6\text{Me}_{12}$ was collected by preparative vpc and identified by nmr and mass spectroscopy. Cleavage with iodine led to the unstable diiodide(II), which was not isolated but was converted to the isolable dihydride(III) and permethylhexagermane(IV). The dihydride was collected on the vpc and characterized by nmr and mass spectroscopy. The $\text{Ge}_6\text{Me}_{14}$ was likewise collected on the vpc and characterized by elemental analysis, nmr and mass spectroscopy.

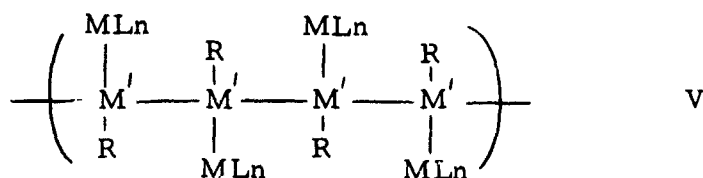


Evidence given in the Russian paper included infrared spectra, nmr, molecular weight (cryoscopic), elemental analysis and the sharp melting point. Elemental analysis and infrared data are not very useful for distinguishing between single compounds and mixtures of linear and cyclic polygermanes. The nmr showed only one signal. Molecular weight data was accurate to about 3%. The sharp melting point is good evidence for the presence of only one compound.

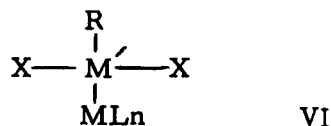
This work will probably be repeated at a later date. It appears that the products most often arrived at were high polymers of germanium plus traces of various chlorogermanes. If $\text{Ge}_6\text{Me}_{12}$ is the thermodynamically favored product, the reaction could probably be improved by a longer reaction time at higher temperature, using Li (1% Na). A new system for crystallization is also needed.

Hydridotin Transition Metal Complexes

For some time researchers in our laboratory have believed that the most likely high temperature superconductors would be polymers of Group IV metals with pendant transition metal units at regular intervals.^{4, 5} In such materials (V) the polymer would form a conduction band, with the transition metal units serving as sources of conduction electrons.



Such polymers also present a feasible synthetic route, since they could arise from the coupling of simple monomer units (VI), and careful regulation of chain length would not be necessary. The strength

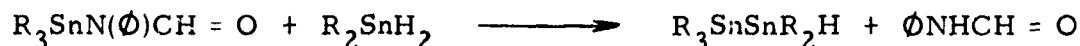


and oxidative stability of the tin-transition metal bond, the availability of simple organotin compounds, and the fact that Sn-Sn coupling reactions are known makes tin the logical choice for initial work.

A very useful method of forming the tin-tin bond is the coupling of tin hydrides with an amine. This reaction may lead to a polymer or a cyclic compound, and in the case of monomeric units like VI, a cyclic product is quite likely.

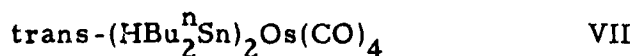


A more selective coupling reaction has been developed by Creemers and Noltes,⁶ utilizing the reaction of an N-phenylformamidotin compound with a tin dihydride.

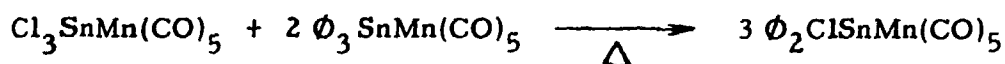
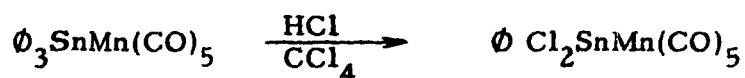
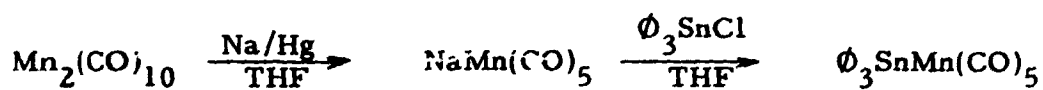


This reaction has been used to produce a number of short linear polystannanes.⁶

Prior to recent work in our laboratory by Don Murphy, Dr. Hoyano and myself, tin hydrides bonded to transition metals were unreported in the literature and were thought to be quite reactive and unstable with respect to self condensation with elimination of H_2 . Working with a model system of tin-manganese compounds prepared by Gorsich,⁷ I attempted to prepare such hydrides by reduction of the corresponding chlorides using lithium aluminum hydride, lithium borohydride and diborane. These reducing agents are apparently too potent, as only decomposition products were observed. During the course of this work, Don Murphy demonstrated the utility of diisobutylaluminum hydride for such reductions, and was able to prepare the compounds VII and VIII.⁸

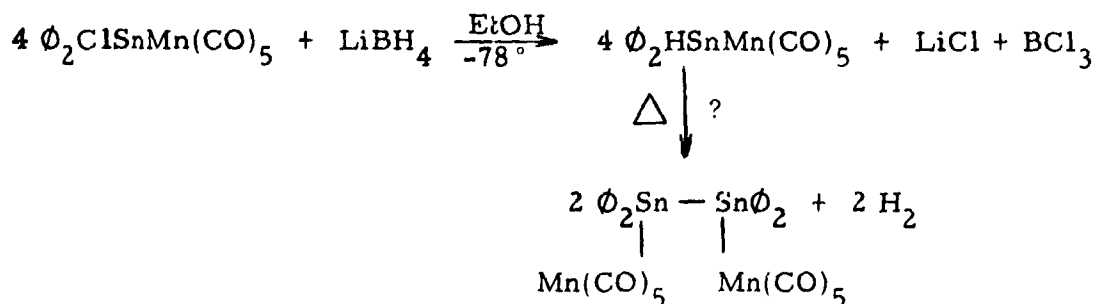


Initial studies of hydridotin transition metal complexes were begun with the Gorsich compounds.⁷ Triphenyltinmanganese pentacarbonyl was prepared from $\phi_3\text{SnCl}$ and $\text{NaMn}(\text{CO})_5$. Selective halogenation was accomplished with either Cl_2 or anhydrous HCl . The most useful derivative, $\text{Cl}\phi_2\text{SnMn}(\text{CO})_5$, was unobtainable by direct halogenation but could be prepared by a redistribution reaction. All of the tin-manganese compounds prepared are air stable in the crystalline state, but are somewhat light sensitive. Oxidative decomposition is prevalent in solution, particularly as the number of $\text{Mn}(\text{CO})_5$ groups around the central tin is increased. The reactions utilized are as follows.



This last redistribution reaction did not go very well, giving only 40-50% yield (lit.⁷ reported 86%) of a low melting impure product requiring several recrystallizations. An attempt to prepare $\phi_2\text{ClSnMn}(\text{CO})_5$ by reaction of $\text{Mn}(\text{CO})_5^-$ with one equivalent of $\phi_2\text{SnCl}_2$ resulted mainly in $\phi_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$. Jetz et. al.^{9a} indicated that overnight reaction is necessary to avoid getting the bis-manganese compound. A lower reaction temperature might also be advantageous.^{9b}

Early attempts to convert the chlorides to hydrides involved reduction of $\phi_2\text{ClSnMn}(\text{CO})_5$ with LiAlH_4 , LiBH_4 and B_2H_6 . Gas evolution was frequently observed upon mixing the reactants, or upon heating to room temperature if the reaction was done at -78° . It was originally felt that the hydride might be stable at low temperature, but couple at higher temperature.



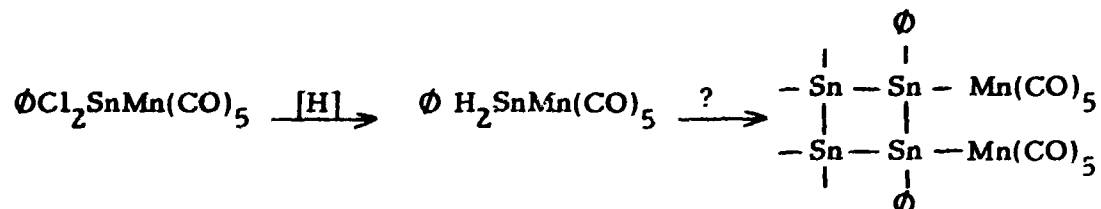
Reaction products were observed by TLC, but early results were not conclusive due to unsuitable plates. Later results on suitable plates (.25mm silica) were more conclusive and reproducible. The solutions always darkened some, turning brown if air was present. All initial studies were done on a very small scale and no products were isolated, but most often the reactions resulted mainly in dark products that did not move on silica. It was concluded that the reducing agents were too potent and probably led to decomposition. Don Murphy later found that both $\text{NaBH}_4/\text{EtOH}$ and $\text{LiAlH}_4/\text{THF}$ attacked the tin-manganese bond, but that diisobutylaluminum hydride in heptane solution was a suitable reducing agent even at room temperature.



Using this medium, the product could be formed in good yield and purified by passing the reaction mixture through a degassed silica column, followed by distillation at reduced pressure. The hydride was collected as a colorless oil with a retention time of ~ 2 minutes on the vpc (190° , 5' 10% carbowax column).

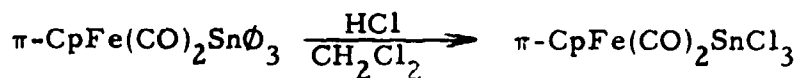
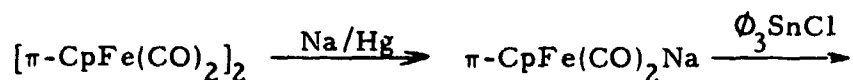
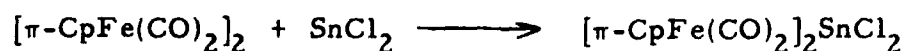
Attempted reduction of the dichloride $\phi\text{Cl}_2\text{SnMn(CO)}_5$ with $i\text{-Bu}_2\text{AlH}$ resulted in a dark solution. Chromatography on a silica column with benzene resulted in a product having several volatile components on the vpc (the hydride might decompose on the column), and nmr indicated that no Sn-H was present. Repeating the reduction at -78° in THF led to an orange solution, and chromatography resulted in a yellow product which precipitated from benzene in air. Preparative TLC led to a yellow residue

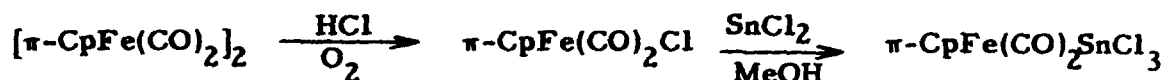
for which the nmr was inconclusive. The dihydride may have formed and decomposed to a cyclic oligomer.



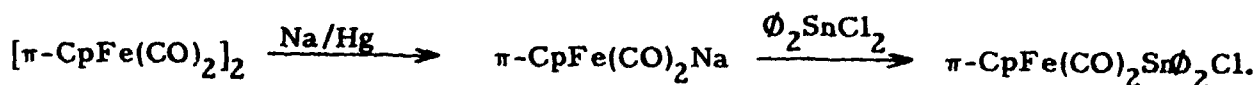
Dr. Hoyano has prepared the bis-(manganese pentacarbonyl)tin dihydride, analogous to the known germanium compound.¹⁰

With $\phi_2\text{HSnMn(CO)}_5$ completely characterized, attempts were made to synthesize hydridotin compounds of other transition metals. Due partly to the relatively low cost of starting materials, tin-iron compounds were the next to be considered. Previous workers had met with failure in attempts to synthesize $[\pi\text{-CpFe(CO)}_2]_2\text{SnH}_2$ ^{1,11} and $\pi\text{-CpFe(CO)}_2\text{SnH}_3$ ¹ by reduction of the corresponding chlorides with LiAlH_4 . My efforts to make $[\pi\text{-CpFe(CO)}_2]_2\text{SnH}_2$ with $i\text{Bu}_2\text{AlH}$ met with similar results, in that the reaction mixture darkened as the temperature was raised from -78° . Several components were noted in thin layer chromatography, but these were not identified.



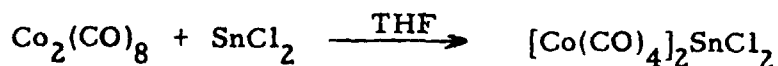


The most stable hydridotin transition metal complexes should be the monohydrides with only one coordinated metal. Preparation of $\pi\text{-CpFe(CO)}_2\text{Sn}\phi_2\text{Cl}$ thus seemed particularly desirable. The previously reported synthesis of this compound¹² was attempted, but yielded only traces of the desired product amid a mass of crude brown material, presumably oxidation products.



Attempts to prepare this compound by the dialkylation of $\pi\text{-CpFe(CO)}_2\text{SnCl}_3$ with ϕMgCl were also unsuccessful. This work will be repeated, and it is expected that the reported synthesis will yield satisfactory results.

Another readily available compound¹³ is bis(tetracarbonylcobalt)tin dichloride, prepared by the insertion of SnCl_2 into $\text{Co}_2(\text{CO})_8$.

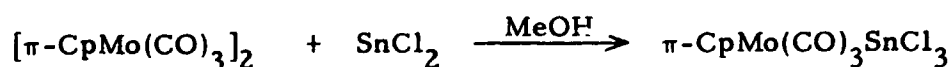
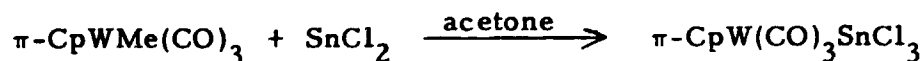


A quick reduction of this compound at room temperature with $i\text{-Bu}_2\text{AlH}$ resulted in a dark solution. After passing the mixture through a silica column, the resulting products showed no Sn-H on the nmr. This reaction will be examined in more detail.

Considerable work will be done in this area in future months. I will continue in attempts to synthesize a number of hydridotin transition metal

complexes, and Dr. Hoyano will be working on corresponding dihydrides. In addition, a model system will be chosen to investigate the chemical behaviour of such compounds, particularly regarding possible coupling schemes. At the present time it appears that $\phi_2\text{HSnMn}(\text{CO})_5$ will be the subject of these studies, but if $\pi\text{-CpFe}(\text{CO})_2\text{Sn}\phi_2\text{H}$ can be prepared it might be used instead.

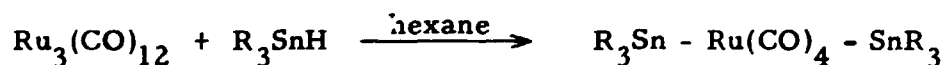
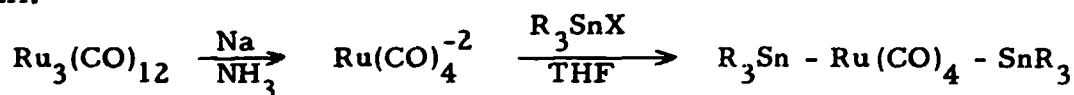
Insertion of SnCl_2 , SnI_2 or GeI_2 has been found to occur readily in a number of dinuclear metal carbonyls containing bridging carbonyl groups. For example, it has been determined¹⁴ that SnI_2 and GeI_2 will insert into the anions $\text{Cr}_2(\text{CO})_{10}^{2-}$ and $\text{W}_2(\text{CO})_{10}^{2-}$ to give the complexes $[(\text{CO})_5\text{M}]_2\text{MI}_2^{2-}$. In addition, SnCl_2 also undergoes the following reactions.¹¹



Reaction of the anions $\pi\text{-CpM}(\text{CO})_3^-$, $\text{M} = \text{Cr}, \text{Mo}, \text{W}$, with trialkyl- or triaryl- Group IV metal halides $\text{R}_3\text{M}'\text{X}$ gives the compounds $\pi\text{-Cp}(\text{CO})_3\text{M-M}'\text{R}_3$.¹⁵ Slow addition of the dihalides $\text{R}_2\text{M}'\text{Cl}_2$ has been found to lead directly to the monohalo compounds $\pi\text{-Cp}(\text{CO})_3\text{M-M}'\text{R}_2\text{Cl}$.¹⁵ In general the chromium compounds are very air and water sensitive, but the molybdenum and tungsten derivatives are quite stable. Some of these compounds might be modified and reduced to give hydridotin complexes of the Group VIa metals.

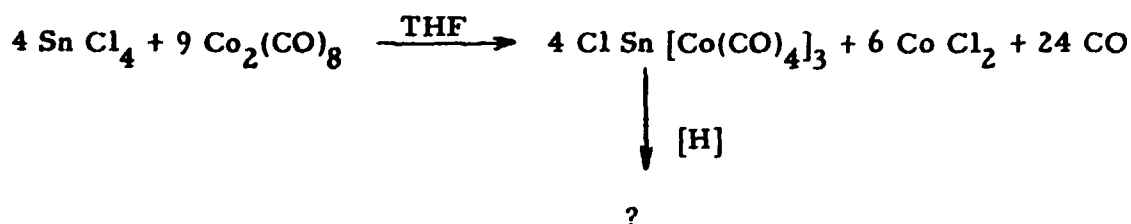
Since the stability of tin-transition metal compounds increases in going down the group,¹⁶ future research in Group VIIa might well involve rhenium analogues of some of the tin-manganese compounds previously discussed.

Owing to relatively inexpensive starting materials, most work in the iron group will probably be done with iron. Some interesting ruthenium compounds have been prepared by Cotton et. al.,^{17, 18} who found that $\phi_3\text{SnCl}$ adds to the anion $\text{Ru}(\text{CO})_4^{2-}$ to give trans-($\phi_3\text{Sn}$)₂ $\text{Ru}(\text{CO})_4$, whereas mixtures of cis and trans species result with trialkyltin chlorides. The same compounds can be better prepared from dodecacarbonyltriruthenium and R_3SnH .



The feasibility of making chlorotin and hydridotin analogues of these compounds may be studied. The monohalotin compounds might be formed directly by using R_2SnCl_2 or R_2SnClH in the above reactions, though the latter is unlikely.

The insertion of SnCl_2 into dicobalt octacarbonyl has already been mentioned. Future studies will be done on this system and related compounds. A novel tin-cobalt compound, tris(tetracarbonylcobalt)tin chloride, has been synthesized in good yield by Patmore and Graham,¹⁹ and an attempt will be made to synthesize the related hydride.



Additional work might eventually be done on chlorotin derivatives of the cobalt complex of bis(diacetylmonoxime-imino)propane described by Do- Murphy.¹

A possibly useful tin-nickel complex has been described,¹³ resulting from the insertion of SnCl_2 into π -cyclopentadienylnickel carbonyl dimer

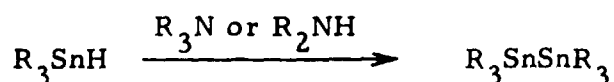
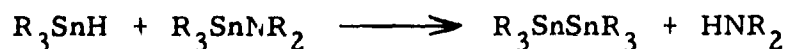


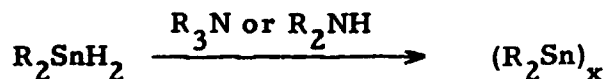
Reduction of this or a related compound might result in a hydridotin nickel species.

Reactions of Hydridotin Transition Metal Complexes

After synthesizing a number of tin hydrides bonded to transition metals we wish to see if their chemical behaviour is the same as simple organotin hydrides, and in particular if these compounds are susceptible to known methods of tin-tin coupling.

Reaction of a tin hydride with a tin-nitrogen species or an amine can lead to formation of a tin-tin bond. For example =

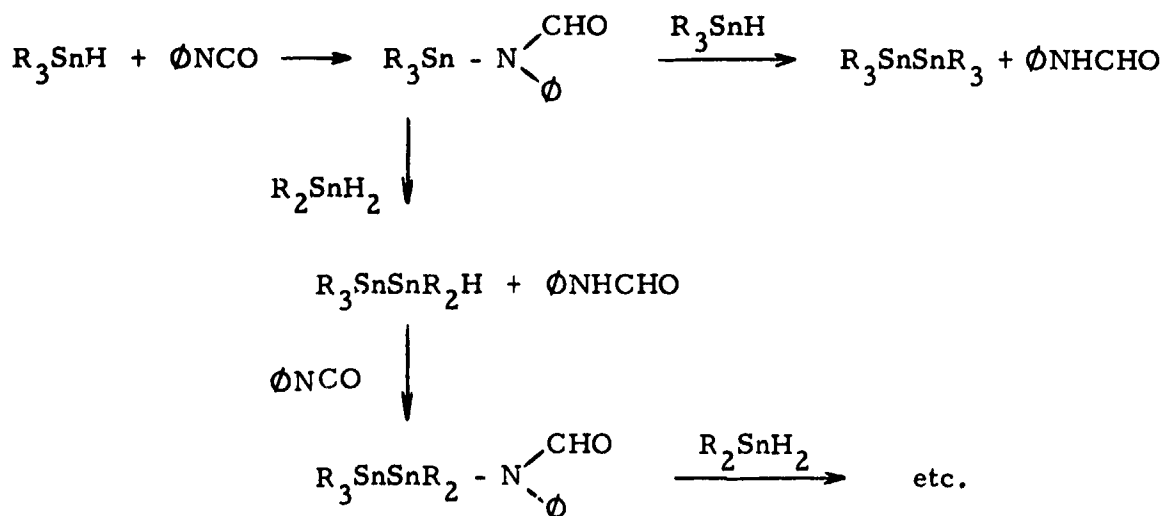




It has also long been known that organotin hydrides add to compounds containing olefinic²⁰ or acetylenic²¹ unsaturation, and it was subsequently demonstrated^{22,23} that trialkyl- or triaryltin hydrides would add to the carbon-nitrogen bond of aryl isocyanates to form trialkyl(N-phenylformamido)-tins.

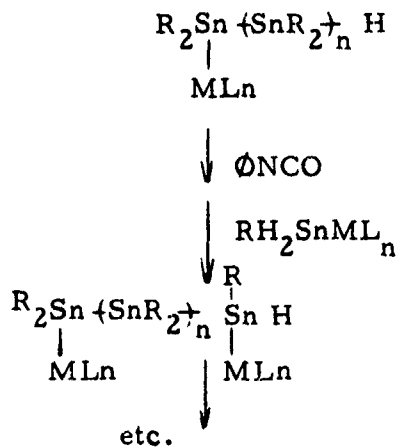
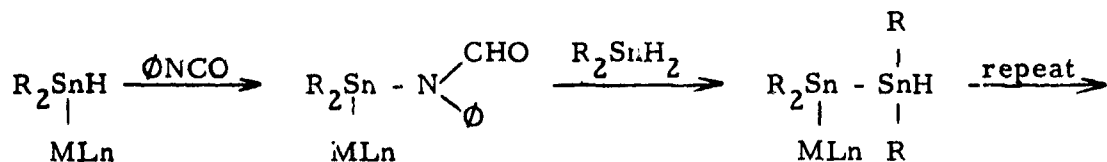
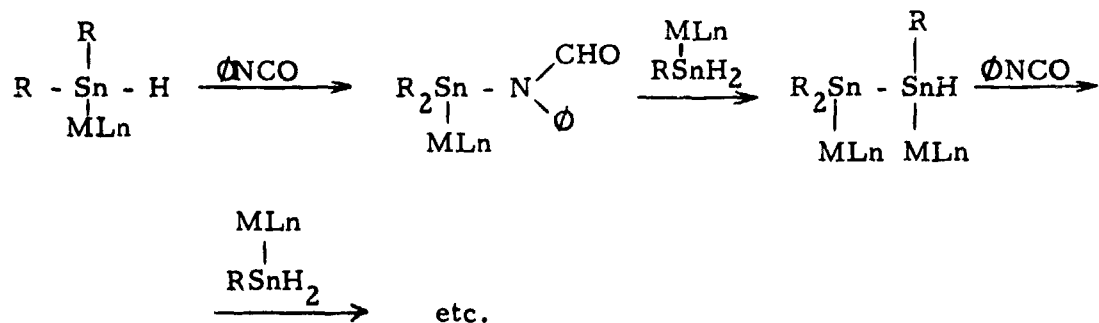
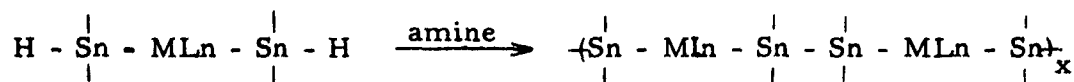
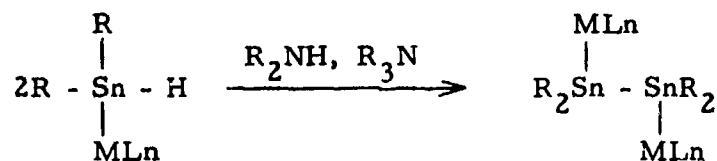
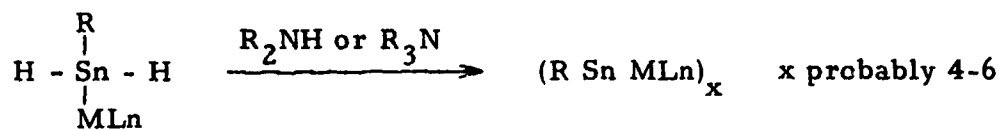


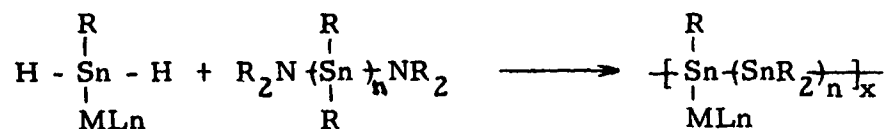
Creemers and Noltes⁶ showed that these reactions could be combined to obtain ditin monohydrides, which could be used subsequently to form a variety of short symmetrical or unsymmetrical tin chains.



If hydridotin transition metal complexes will undergo these reactions, then a number of interesting polymers containing either alternating tin and transition metal units or metal groups pendant off tin chains could be

formed. Note that simple dihydrides probably would not polymerize linearly but would form cycles. Longer units are needed for polymerization.





Experimental

All reactions were carried out under an argon atmosphere. Vpc results are on the Varian Autoprep 705 with Se-30 column for germanium compounds, and Hewlett Packard 5750 with 5' 10% carbowax column for tin compounds. Nmr spectra were recorded on the Varian T-60.

Dodecamethylcyclohexagermane

Cooke procedure.¹ .90 gm Li metal chips are washed in hexane and placed in 9 cc THF. 2 cc Me_2GeCl_2 is added over a one hour period at 50-55°, and the solution is stirred three hours while monitoring the reaction on the vpc. The mixture is diluted in ether, filtered, stripped and passed through a silica column to remove chlorogermanes and insoluble polymers. The resulting oil is taken up in acetone and treated with water to the cloud point. Crystallization in the refrigerator reportedly yields 420 mg product (24%).

The first time I attempted this procedure the oil eluted from the column contained a number of products by vpc, not all soluble in acetone. Nothing crystallized from acetone/water.

.45 gm Li chips containing 1% Na were placed in 6 cc THF and 1 cc Me_2GeCl_2 was added over 20 minutes. After stirring 2-1/2 hours at room

temperature, the mixture was worked up as above, the resulting oil being dissolved in hot acetone and then cooled. A tiny bit of precipitate was removed, and the solution concentrated to give a crystalline product, 95% pure (vpc) and identical to that prepared by Dr. Cooke.

The procedure was repeated, adding the Me_2GeCl_2 over 10 minutes and stirring 1-1/2 hours at 45° and one hour at 60° . After workup the product was not entirely soluble in acetone but was in CHCl_3 . Slow evaporation yielded only a gummy substance.

The Russian procedure was followed using $\text{Li}(1\%\text{Na})$ instead of powdered lithium. .9 gm Li chips were placed in THF at $40-46^\circ$ and over a period of one hour was added 6.5 gm (4.37cc) Me_2GeCl_2 . The mixture was stirred 1-1/2 hours, diluted with ether and filtered. The turbid yellow filtrate was stripped and the residue extracted with 95% EtOH. A slimy white material with an acrid odor was left behind. Vpc showed that this contained no $\text{Ge}_6\text{Me}_{12}$. The ethanol was filtered hot and set aside, but nothing crystallized even with addition of water. This solution was evaporated, and addition of hexane caused a yellow coagulum to form. This was taken up in CHCl_3 and the solvent evaporated to give an acrid smelling glassy solid (crude mp $210-280^\circ$). When ground up, it fused together again on standing. Vpc of this glassy solid indicated some $\text{Ge}_6\text{Me}_{12}$ and several other components of shorter retention time. The product was triturated with CHCl_3 , passed through a silica column and again evaporated to a solid mass, mp $245-260^\circ$. Crystallization from several solvent systems

failed, and the material would not move on silica in benzene or hexane. The solid was ground up and put under a 20 mm vacuum for 10 hours at 80°C, after which time it no longer coagulated (mp 230-275°). This is apparently a polymer or mixture of polymers (with some $\text{Ge}_6\text{Me}_{12}$ present).

Li (.225 gm) was stirred in 4 cc refluxing THF. 1 cc Me_2GeCl_2 was added over one hour and the solution refluxed 2-1/2 hours. After diluting, filtering and stripping, a strong smelling liquid product was obtained. Vpc indicated some $\text{Ge}_6\text{Me}_{12}$ and several compounds of short retention time. After passing through a silica column, the residue yielded only a few mg of slimy polymeric material.

The Russian procedure was repeated with Li (1% Na) and stirring the reaction mixture 7-1/2 hours at 40-46°. Diluting, filtering and evaporation of the solvent led to an acrid yellow oil/solid, which was taken up in CHCl_3 . Some insoluble white material was filtered off, and slow evaporation of the filtrate with addition of hexane yielded no precipitates. The solution was stripped and taken up in hot acetone, leaving behind a gummy white mass. The acetone solution contained 6-8 products by vpc, including $\text{Ge}_6\text{Me}_{12}$ as a major one, but it could not be recovered by crystallization. Chromatography followed by preparative vpc would probably be the best procedure.

The Cooke procedure was repeated again. The reaction mixture was filtered and stripped to a yellow solid/oil. Addition of hexane caused a large mass to coagulate (only partly soluble in CHCl_3), and this contained no $\text{Ge}_6\text{Me}_{12}$. The hexane-soluble products were chromatographed, and

vpc of the eluant indicated at least 10 components, with $\text{Ge}_6\text{Me}_{12}$ being the largest of several major ones. Attempts to induce crystallization from several solvent systems failed, but masses of gummy white material were recovered at several stages while studying the coagulated substance formed above. We must conclude that a large portion of the germanium was converted to high polymers.

(Triphenyltin)manganese Pentacarbonyl

Sodium amalgam (200 gm, 1%) was prepared and mixed with 7.8 gm (.02 mole) $\text{Mn}_2(\text{CO})_{10}$ in 120 cc THF. The mixture was stirred at room temperature for one hour, at which time the green anion solution was added (needle syphon) to 15.2 gm (.0395 mole) $\text{C}_6\text{H}_5\text{SnCl}$. After stirring at room temperature for 30 minutes the solution was stripped to one half its volume and added to 300 cc ice water. The large mass of greenish-white solid precipitate was filtered and dried. Extraction of the solid with boiling n-hexane and concentration of the hexane filtrate led to a first crop of 10.3 gms, mp 147-149°. A second crop contained a brown impurity which was removed with celite. Total 15.2 gms (71%).

(Trichlorotin)manganese Pentacarbonyl

Chlorine was bubbled through a solution of 6 gms $\text{C}_6\text{H}_5\text{SnMn}(\text{CO})_5$ in 100 cc CCl_4 for 30 minutes. A white solid precipitated. Excess Cl_2 was removed at the water aspirator and the solution was heated to reflux and filtered while hot (additional CCl_4 needed to dissolve product). The filtrate was concentrated to ~150 cc and chilled. The product was collected, 3.97 gms (86%), mp 164-66° (decomp.).

(Phenyldichlorotin)manganese Pentacarbonyl

Anhydrous HCl was bubbled through a solution of 1.0 gm $\phi_3\text{SnMn(CO)}_5$ in 60 cc CCl_4 for one hour while keeping the reaction temperature at 0° . The solvent was evaporated at $\sim 15^\circ$ under vacuum, and the residue was extracted with boiling n-hexane. Crystallization led to .58 gm product (68%), mp $81-83^\circ$.

(Diphenylchlorotin)manganese Pentacarbonyl

This preparation did not go as well as reported,⁷ and there was difficulty in getting a pure product (reported mp $97-98^\circ$).

A mixture of 1.05 gm (.0025 mole) $\text{Cl}_3\text{SnMn(CO)}_5$ and 2.75 gm (.005 mole) $\phi_3\text{SnMn(CO)}_5$ was heated at $\sim 150^\circ$ under argon for one hour. The residue was taken up in boiling n-hexane and filtered through celite. Evaporation to 30 cc and chilling led to an off-white product of 1.407 gm, mp $90-94^\circ$. Second crop .74 gm, mp $87-91^\circ$. Yield 56%.

An attempt to react equimolar amounts of NaMn(CO)_5 and $\phi_2\text{SnCl}_2$ resulted only in the formation of $\phi_2\text{Sn[Mn(CO)}_5\text{]}_2$. Thompson and Graham^{9b} have indicated that the addition should be done at -5° , and Jetz et. al^{9a} found that the solution must stand overnight to avoid formation of the bismanganese product.

A solution of NaMn(CO)_5 prepared from 200 gm 1% amalgam and 7.8 gms (.02 moles) $\text{Mn}_2(\text{CO})_{10}$ in 120 cc THF was slowly added to 13.75 gms (.04 mole) $\phi_2\text{SnCl}_2$. The solution was stirred one hour and stripped to a green oil. This was taken up in hexane and filtered to give a yellow

solution which when chilled gave a precipitate of ~6.8 gm, mp 115-125°. Second and third crops of low melting (60-90°) materials were recovered. The first crop was recrystallized from ethanol to give 4.17 gms of yellow plates of $\phi_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$, mp 130-131°. The second and third crops combined gave 1.8 gm, mp 132-135°. Reported⁷ mp 137-139°.

(Diphenylhydridotin)manganese pentacarbonyl

The first attempts at this reduction were done with LiBH_4 in ethanol. The earliest trials indicated evolution of a gas upon mixing the reactants at -78°, with more gas evolution as the solution heated to room temperature. The solution also became dark with time, and products which originally moved on TLC failed to do so after the reaction mixture had set for several days. When the reduction was done in the presence of air, no products which moved on silica resulted. With reaction at -78° under argon the mixture turned yellow but did not darken. A product resulted which moved at a response of .8-.9 on silica in 16% acetone/hexane.

About .25 gms $\phi_2\text{ClSnMn}(\text{CO})_5$ and excess (10 mg) LiBH_4 were stirred in ethanol at -78° for 1/2 hour and then heated to room temperature for two hours. 2 cc methanol was added to the lemon yellow solution to destroy excess borohydride, and evaporation of the solvent led to a white solid and yellow oil. The residue was taken up in CH_2Cl_2 and filtered (solution turned orange). Nothing crystallized from CH_2Cl_2 /hexane but evaporation led to a yellow oil which turned solid (impure, mp 60-90°). TLC indicated a mixture, with most of the products not moving on silica. Some unreacted starting material was also present.

10 mg $\phi_2\text{ClSnMn(CO)}_5$ was placed in THF at -78° and to this was added .1 cc B_2H_6 (1M in THF). After stirring 1/2 hour and heating to room temperature 1/2 hour, the solution was light yellow. This was stripped on the vacuum line to an orange oil, which was taken up in CH_2Cl_2 and chromatographed in benzene. TLC showed several components to the dark mixture.

252 mg $\phi_2\text{ClSnMn(CO)}_5$ were placed in 5 cc degassed hexane under argon, and to this was added over 10 minutes at room temperature 500 μl 1.04 N i-Bu₂AlH in heptane. The mixture was stirred one hour and passed through a silica column on benzene. After stripping the product to an orange oil, the hydride was distilled (molecular still) $130-155^\circ$ (275-300 μ). Vpc at 190° on a 5' 10% carbowax column indicated 80-90% purity (retention time $\sim 2-1/2$ minutes). Yield .18 gm (76%). Thin layer response $\sim .3$ in hexane on silica. Nmr in CDCl_3 ²⁴ indicates Sn-H at 360 Hz. Infrared $\nu(\text{Sn-H})$ 1795 cm^{-1} . This compound was also prepared by Don Murphy⁸ and the elemental analysis was excellent.

(Phenyldihydridotin)manganese Pentacarbonyl

10 mg $\phi\text{Cl}_2\text{SnMn(CO)}_5$ was reacted with excess (1 mg) LiBH_4 in EtOH at -78° . After stirring one hour the yellow solution contained one product which moved on silica in acetone/hexane. Addition of methanol followed by heating the solution in air caused no color change. The solution was evaporated and the residue extracted between CH_2Cl_2 and water. A precipitate formed, apparently a polymeric sludge. No useful products were observed in the CH_2Cl_2 solution.

To 46 mg (.1 mmole) $\text{OCl}_2\text{SnMn}(\text{CO})_5$ in 1-2 cc degassed hexane was added 193 μl $i\text{-Bu}_2\text{AlH}$ (.2 mmole, 1.04 M in heptane) over a period of 5 minutes. After stirring one hour the almost black solution was passed through a silica column on benzene. The product moved as a yellow band, and a number of volatile components were present by vpc. Nmr indicated no Sn-H.

Repeating the above in THF at -78° and stirring 2-1/2 hours resulted in a yellow solution which turned orange at room temperature. TLC indicated a large amount of material with a response of .8 on silica in benzene. After passing the mixture through a silica column, the yellow eluant precipitated as it hit the receiving flask (in air). Thin layer analysis was the same, and was unchanged four days later. Preparative TLC gave an estimated 10 mg yellow oil. Nmr in CDCl_3 was inconclusive, but a small peak was observed at 318 Hz.

Bis(π -cyclopentadienyldicarbonyliron)tin dichloride

5 gms (14.1 mmole) $[\pi\text{-CpFe}(\text{CO})_2]_2$ and excess (10 gm, 53 mmole) anhydrous SnCl_2 in 250 cc methanol and 25 cc EtOAc were refluxed 20 hours. On cooling an orange product precipitated which was washed in methanol, ether, and recrystallized from methanol to give orange needles. Recrystallization from toluene/pet ether gave 3.8 gms, mp $163\text{-}165^\circ$ (50%).

Reduction of $[\pi\text{-CpFe}(\text{CO})_2]_2\text{SnCl}_2$

To a solution of 544 mg (1 mmole) $[\pi\text{-CpFe}(\text{CO})_2]_2\text{SnCl}_2$ in THF at -78° was added 1.93 ml (2 mmole) $i\text{-Bu}_2\text{AlH}$ in heptane. The resulting red

solution was stirred two hours and heated to room temperature, where it turned dark red-brown. TLC indicated no products that moved on silica in C_6H_6 . The solution did pass through a large degassed silica column, with a red eluant being slowly removed by benzene. Nothing moved on TLC, but a cruddy brown precipitate formed on sitting overnight. This brown solid did not melt.

When the reaction was done at room temperature, the solution turned dark red-brown upon addition of the hydride. After two hours, TLC showed no products, but chromatography on a degassed column led to a brown eluant containing at least five components by TLC.

Alkylation of π -CpFe(CO) $_2$ SnCl $_3$

2 mmoles (.804 gm) π -CpFe(CO) $_2$ SnCl $_3$ was placed in 50 cc THF. While cooling in ice. 4 mmoles ϕ MgCl (in THF) was added, changing the solution from light orange to dark red. After stirring at room temperature for three hours the solution was stripped and the residue taken up in CH $_2$ Cl $_2$ and filtered (celite) and stripped to a red oil. Attempts to crystallize this oil from a variety of solvents led only to dark high melting materials, apparently oxidation products.

Bis(tetracarbonylcobalt)tin Dichloride

Co $_2$ (CO) $_8$ (1.03gm, 3 mmole) and .57 gm (3 mmole) anhydrous SnCl $_2$ were placed in 25 cc THF and stirred at room temperature for 20 minutes. The solution was stripped and the residue taken up in a minimum amount of dichloromethane. After filtering and cooling (ice), slow addition of pentane precipitated an orange-red solid (also a second crop). Recrystallization from CH $_2$ Cl $_2$ /pentane yielded .7 gms product (44%) mp 106-108° (decomp.)

Reduction of $[\text{Co}(\text{CO})_4]_2\text{SnCl}_2$

.088 gm (.257 mmole) $[\text{Co}(\text{CO})_4]_2\text{SnCl}_2$ in degassed benzene was treated with .55 mmoles $i\text{-Bu}_2\text{AlH}$ (1.04 M in heptane) at room temperature. The solution turned dark brown immediately, and after stirring one hour the mixture was stripped and the residue taken up in benzene and passed through a silica column. Nmr indicated no Sn-H.

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Semi-Annual Research Report

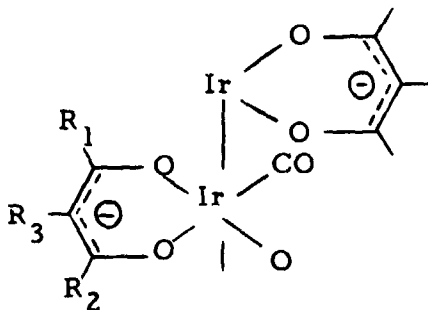
by

Lawrence Libit

December, 1971

Introduction

As part of our effort to produce compounds and crystals that contain a metallic spine surrounded by polarizable organic groups as candidates for organo-metallic superconductors, we have investigated the iridium dicarbonyl acetylacetonate system $[\text{Ir}(\text{CO})_2\text{AcAc}]$.¹ The $\text{Ir}(\text{CO})_2\text{AcAc}$ system has a crystal packing pattern that permits strong metal-metal bond interaction (the internuclear distance in a given chain is 3.20 \AA).²



The crystal pattern is best thought of as a series of iridium chains separated by organic spacers (the AcAc and CO moieties). Thus, it's possible to study two important aspects of W. A. Little's theory of superconductivity.³ First, increased iridium chain separation should reduce crystal conductivity parallel to the metallic spines as the screening of

electron-hole interaction by proximate iridium chains is substantially reduced, producing more localization of electronic charge and thereby reducing conductivity. To experimentally test this hypothesis the size of R_1 , R_2 , or R_3 can be varied to change the interchain distance and conductivity can be measured as a function of interchain distance (determined by X-ray analysis). The second aspect of Little's theory that can be tested in this system is the effect of a proximate polarizable group (i. e. a dye) on the conducting properties of such a metallic spine. Thus the attachment of a dye at C_1 , C_2 or C_3 of the acetylacetone in the $\text{Ir}(\text{CO})_2\text{AcAc}$ complex is experimentally feasible and of extreme importance.

The experimental work described herein is directed to both of the above points. The first part of this report describes the synthesis of several acetylacetones in which the size of the C_1 and C_3 substituents has been varied. The second part describes the successful synthesis of a 3-azulyl acetoacetate ligand and a preliminary attempt to place azulenes at C_1 and/or C_3 in an acetylacetone ligand.

Part A. The Synthesis of 1,3-diketones.

Table I displays the 1,3-disubstituted acetylacetones synthesized during the term of this report. The method used was originally developed by Hauser et al.⁴ and involves the base (sodium amide or sodium hydride) catalyzed condensation of a ketone with an ester:

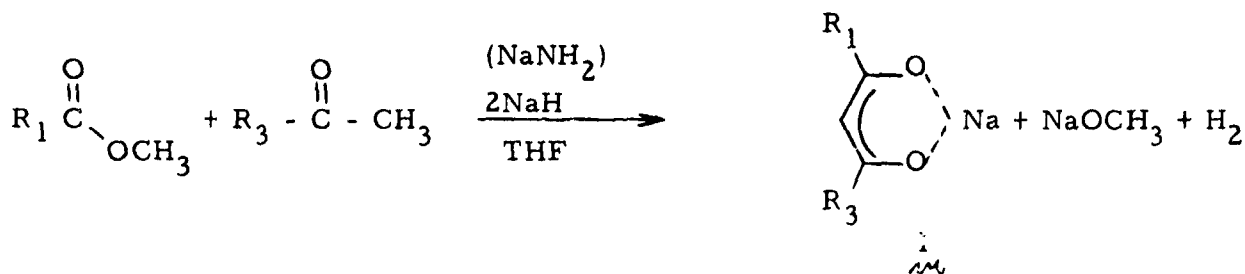
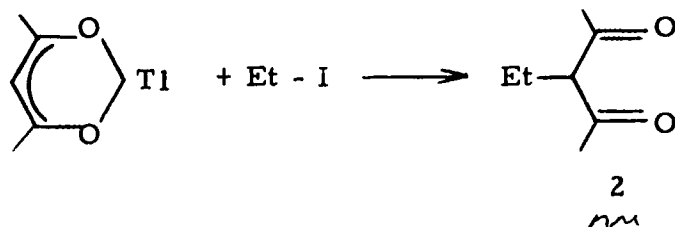


Table I

<u>Ester</u>	<u>Ketone</u>	<u>Base</u>	<u>Product</u>	<u>R₁</u>	<u>R₃</u>
methylpropionate	methylethyl	NaH	1a <u>w</u>	ethyl	ethyl
ethylbutyrate	methylpropyl	NaNH ₂	1b <u>m</u>	propyl	propyl
ethylisovalerate	methylisobutyl	NaNH ₂	1c <u>m</u>	isobutyl	isobutyl
ethylhexanoate	methylpentyl	NaNH ₂	1d <u>m</u>	pentyl	pentyl
methylbenzoate	methylphenyl	NaNH ₂	1e <u>m</u>	phenyl	phenyl
2-carbomethoxy naphthalene	methylisobutyl	NaH	1f <u>m</u>	naphthyl	isobutyl

The middle carbon (C₂) of acetylacetone can also be substituted using the thallium reagent developed by E. C. Taylor and A. McKillop.⁵ This reaction was experimentally investigated and the 3-ethyl derivative of acetylacetone was produced in >75% yield. Thus all the carbons in the AcAc

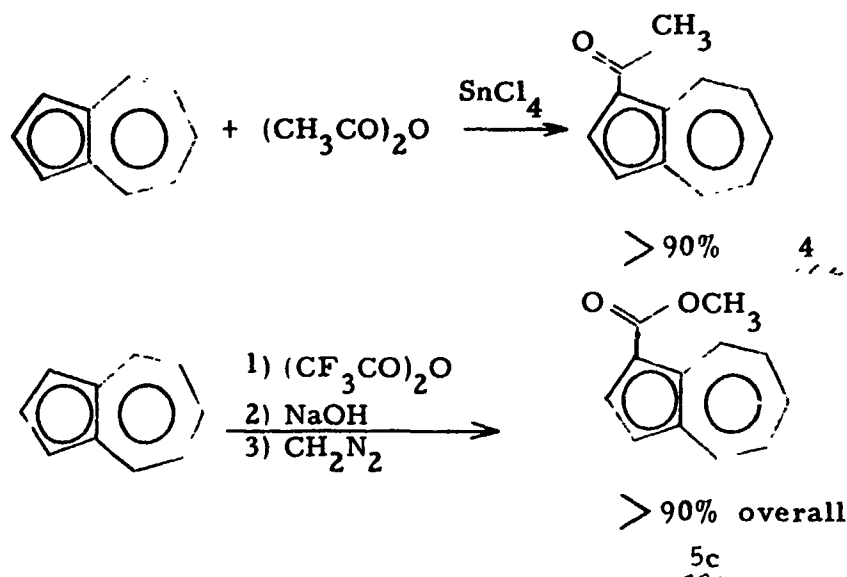


ligand can be readily substituted. For a report on the iridium complexes derived from the ligands see the research report submitted by M. MacLaury.

At this point we turned our attention to the synthesis of an acetylacetone ligand with R₁, R₂ or R₃ replaced by an organic dye. Our first choice of a dye was the azulene nucleus itself. We chose azulene for the dye because it is a neutral molecule (as opposed to the cyanine series) and because it contains an optical transition that can be shifted and intensified by the proper choice of substituents.⁶ Part B records our attempts to introduce azulene itself into an AcAc ligand.

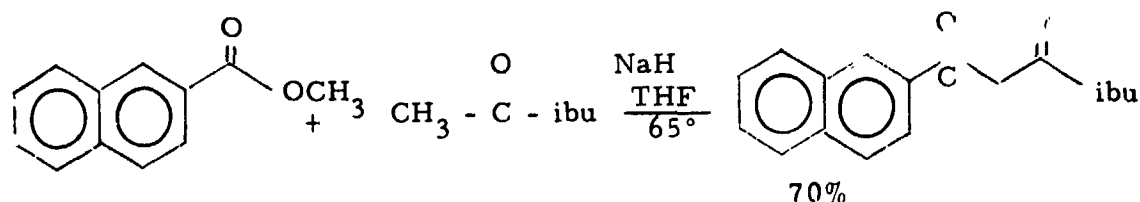
Part B. Preliminary Report on the Synthesis of Azulylacetylacetones

In an attempt to apply the Hauser β-diketone synthesis in the azulene system we prepared 1-acetylazulene and 1-carbomethoxyazulene from azulene.⁷



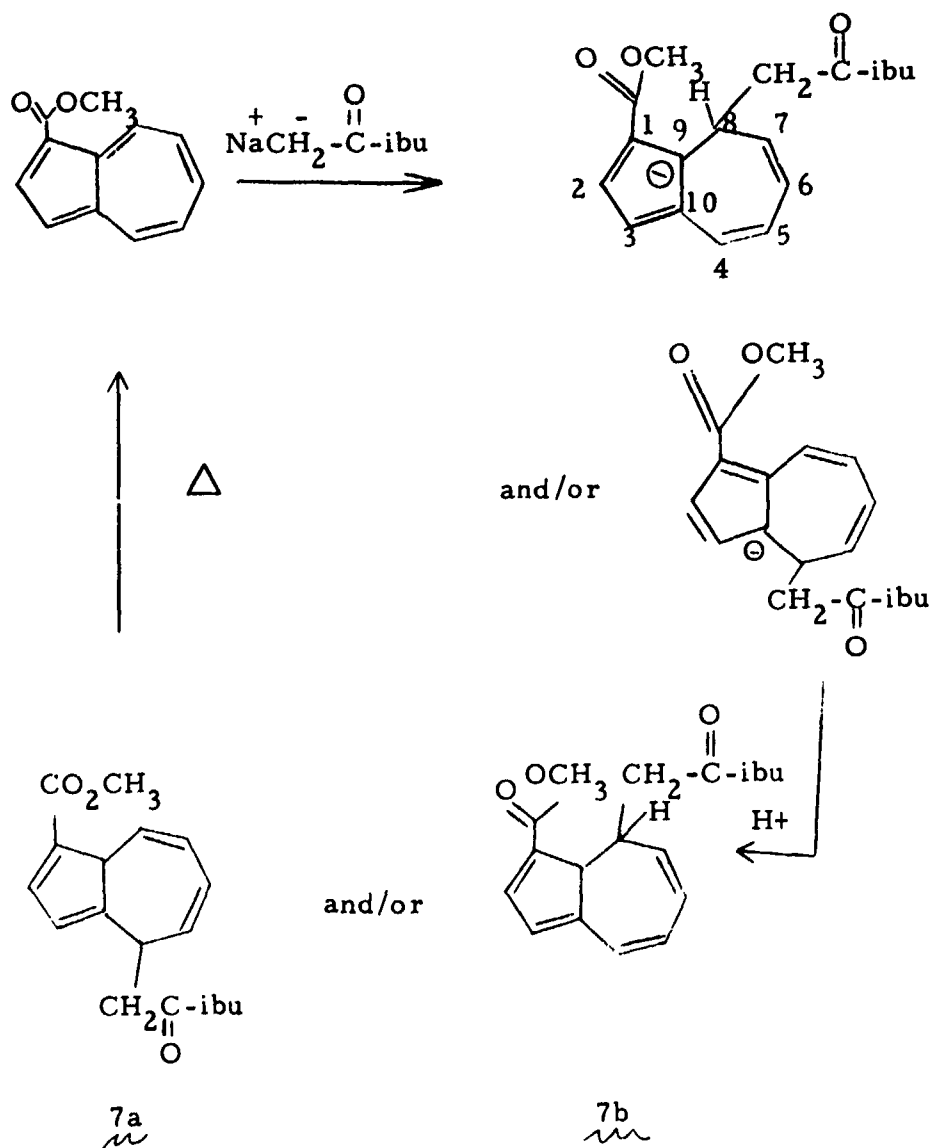
1. Attempt to condense a methyl ketone with 1-carbomethoxyazulene.

An examination of Hausers work revealed that acetone and methylisobutyl ketone produced the highest yields of β -diketones in their respective base (NaH) catalyzed condensations with esters. In a model experiment we found a smooth condensation of methylisobutylketone with 2-carbomethoxy-naphthalene in THF to produce the desired β -diketone in 70% purified yield.



Under these same conditions the reaction of methylisobutylketone with 1-carbomethoxyazulene produced no β -diketone. Instead the enolate of methylisobutylketone apparently adds to the azulene nucleus and this adduct has been shown to thermally revert (essentially quantitative) to 1-carbomethoxyazulene on vpc analysis. The 1-carbomethoxyazulene is

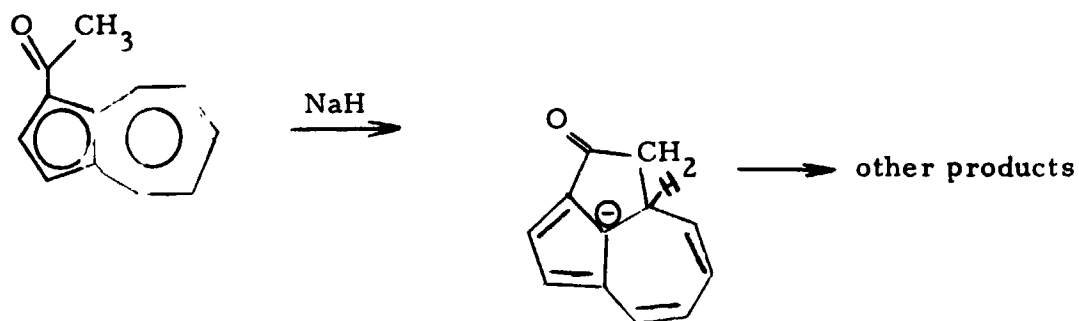
consumed within minutes of the addition of the ketone as judged by vpc analysis. After aqueous work-up the nmr spectrum showed an intact methyl ester chromophore and no low field azulenic absorbance. After work-up vpc analysis revealed only 1-carbomethoxyazulene which could only arise from thermolysis of the reaction product on the vpc column. Thus, the above observations can be described in the following manner:



The same experimental results were obtained in the attempted base catalyzed condensation of acetone with 1-carbomethoxyazulene.

2. Attempts to condense 1-acetylazulene with esters.

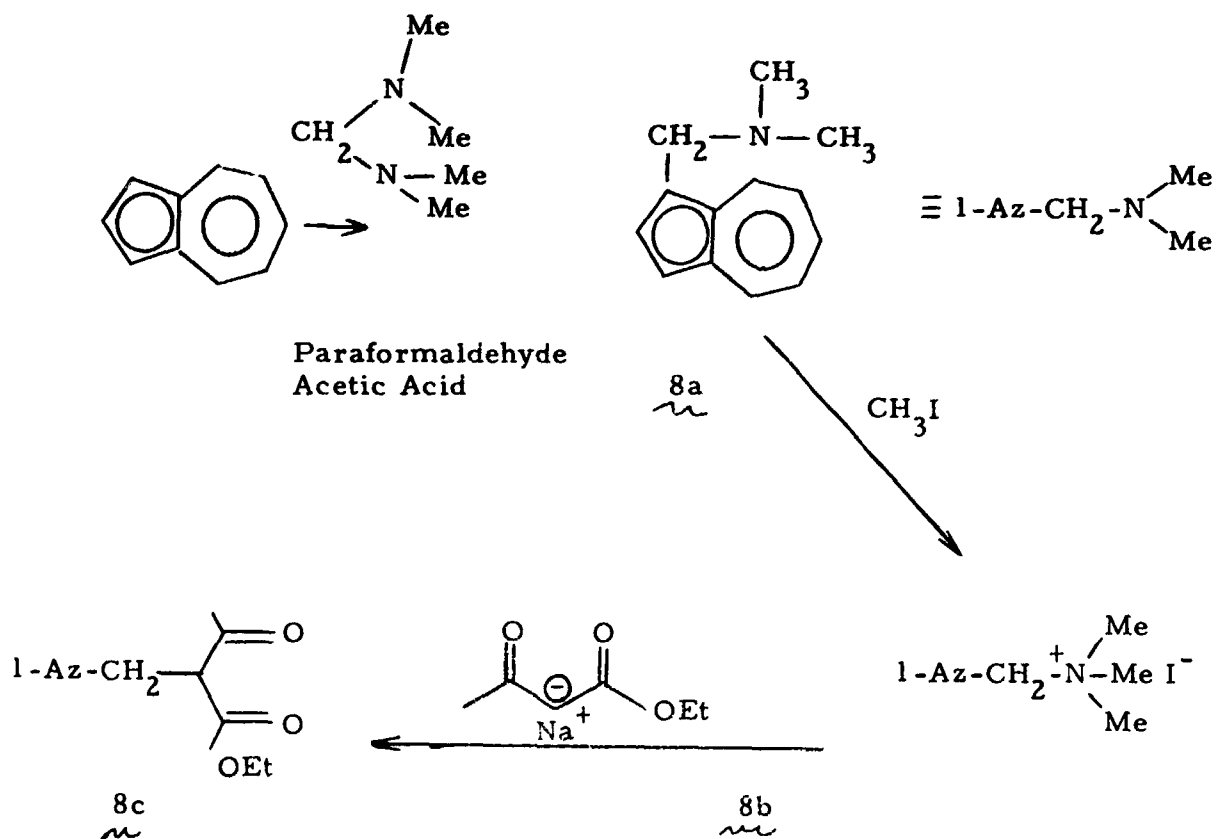
The addition of 1-acetylazulene to a mixture of an ester (methylbenzoate or ethylacetate), sodium hydride and THF (or DMSO) results in the rapid consumption of the ketone and produces none of the desired β -diketone. Protonation of the reaction mixture does not regenerate 1-acetylazulene, thus we are producing a reactive enolate or the azulene ring is irreversibly attacked by sodium hydride:



These preliminary results confirm the sensitivity of the azulene ring to nucleophilic attack and we are considering other methods to achieve our synthetic goal in this system (see end of report).

3. The synthesis of a 3-azulyl acetoacetate ligand.

A search of the literature on azulene chemistry revealed the existence of an azulene acetoacetate.⁸ We achieved the synthesis of this ligand as outlined below.



At present we are investigating the complex formation of this ligand with $\text{Ir}(\text{CO})_3\text{Cl}$.

Conclusion

We have accomplished the synthesis of several substituted (at C_1 , C_2 and C_3) acetylacetones and we have prepared several $\text{Ir}(\text{CO})_2\text{AcAc}$ complexes of these ligands. The conductivity and X-ray structure of these compounds is presently being determined to correlate the interchain distance with single crystal conductivity parallel to the iridium chain. We have prepared a dye (azulene) containing AcAc and we should produce other dye containing ligands during the next six months to check the effect of a polarizable molecule on the single crystal conductivity.

Experimental

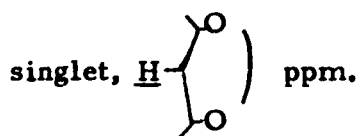
Dipropionylmethane. (1a)^{4a}
ma To a solution of methylpropionate (35.2g, 400 mmole), ether (200 ml) and sodium hydride (9.6g, 400 mmole; washed free of mineral oil with three 50 ml portions of ether) was added at room temperature, under nitrogen, methylethyl ketone (14.42g, 200 mmole) in 50 ml ether. The ketone was added over one hour and the resulting mixture stirred four hours under nitrogen until hydrogen evolution ceased. Additional ether was added during the reaction to keep a fluid mixture. Excess sodium hydride was destroyed by the addition of ethanol (20 ml) at -78°. At 0-5° a mixture of ice-water and concentrated hydrochloric acid (enough to obtain a neutral pH) was then added and the aqueous phase was washed with ether (3 x 100 ml). The ether was washed successively with saturated sodium bicarbonate (50 ml) and brine (50 ml) solutions and dried over magnesium sulfate. The organic extract was filtered and concentrated at reduced pressure to obtain a residual oil. This oil was dissolved in methanol (50 ml) and a hot, filtered solution of cupric acetate monohydrate (40 g) in 400 ml water was added. The mixture was cooled to room temperature and the crystalline copper chelate was collected by filtration.

The crystals were dissolved in 10% sulfuric acid (200 ml) and the resulting aqueous phase washed with ether (3 x 100 ml). The combined organic extracts were washed with saturated brine (50 ml), dried over sodium sulfate (anhydrous), filtered and concentrated to a residual oil

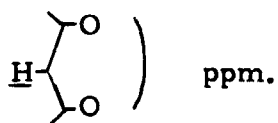
(3.8 g, 24.6 mmole). The oil was distilled (70°/30 mm) to obtain pure dipropronylmethane (3g). The nmr spectrum (CCl_4) was consistent with the desired product, displaying peaks at 1.2 (6H, triplet, $J = 7$ cps, - C - CH_2 - CH_3), 3.4 (0.2H, singlet, $\text{H}_2\text{C} \begin{array}{l} \diagup \text{=O} \\ \diagdown \text{=O} \end{array}$) and 5.4 (0.84, singlet, $\text{H} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array} \text{H}$) ppm.

Dibutylrylmethane (1b) (4b). To a solution of liquid ammonia (300 ml) and ferric nitrate (~500 mg) under argon at -78° was added freshly cut sodium (13.8 g, 0.6 mole). After 30 minutes, the solution was warmed to room temperature as the ammoniac evaporated and 300 ml ether was added to maintain the original volume. When all the ammonia was removed a solution of methylpropyl ketone (51.5 g, 0.6 mole) in ether (50 ml) was added over 15 minutes. Then a solution of ethylbutyrate (69.5 g, 0.6 mole) in ether (50 ml) was added over 10 minutes. After two hours at 35 - 40° the mixture was poured into cold water (~300 ml) and the aqueous phase was neutralized with concentrated hydrochloric acid. The aqueous phase was washed with ether (3 x 100 ml) and the combined organic extracts were concentrated. The residual oil was dissolved in methanol (50 ml); a hot solution of cupric acetate monohydrate (44 g) in water (350 ml) was added and the resulting crystals of the copper chelate were collected by filtration. The crystals were dissolved in 200 ml 10% sulfuric acid and the aqueous phase washed with ether (2 x 100 ml). The

combined organic extracts were dried (Na_2SO_4), filtered and concentrated to a residual oil. Distillation of this oil (b.p. $95^\circ/20$ mm) gave pure product (22 g, 156 mmole, 30% yield). The nmr spectrum (CCl_4) was entirely consistent with the title compound, showing peaks at 1.0 (6H, triplet, $J = 5$ cps, $-\text{CH}_2\text{CH}_3$), 1.4 - 2.0 (4H, multiplet, $\overset{\text{O}}{\parallel}\text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$), 2 - 2.6 (4 H, distorted triplet, $\overset{\text{O}}{\parallel}\text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$) and 5.3 (1 H,



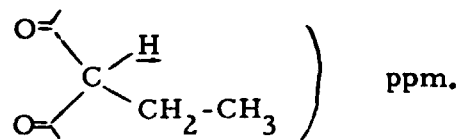
Di-(3-methylbutyl)methane (1c). The title compound was prepared from methyl isobutylketone, ethylisovalerate and sodium amide according to the dibutylrylmethane procedure. Yield: 40%, b.p. 110° at 20 mm. The nmr (CCl_4) spectrum showed peaks at 1.0 (6H, doublet $J=7$ cps $\text{CH}(\text{CH}_3)_2$), 2.2 (3H, multiplet, $\overset{\text{O}}{\parallel}\text{C} - \text{CH}_2 - \text{CH}$) and 5.3 (1H, singlet,



Di-hexanoylmethone (1d). The title compound was prepared according to the procedure described for dibutylrylmethane using methyl pentyl ketone, ethyl hexanoate and sodium amide. Yield: 50%, b.p. 95° at 0.1 mm.

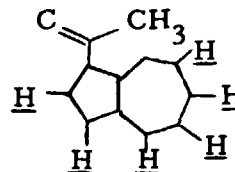
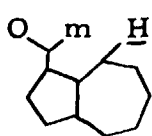
Dibenzoylmethane. (1e) The title compound was prepared from acetophenone, methylbenzoate and sodium amide according to the procedure described for dibutylrylmethane. Yield after crystallization from petroleum ether: 60% (m.p. $76-78^\circ$). The nmr spectrum (CDCl_3) showed signals at 6.8 (1 H, Singlet $\text{H} - \begin{array}{c} \diagup \text{O} \\ | \\ \diagdown \text{O} \end{array} \text{) }$ and 7.4 - 8.2 (10H, multiplet, $2\text{C}_6\text{H}_5$) ppm.

3-ethylacetylacetone (2) ⁵. Thallium (I) ethoxide (5g, 20 mmole) was added to a solution of acetylacetone (2.2g, 22 mmole) and hexane (75 ml), after a few minutes a white precipitate was observed; the solution was chilled and the solvent was removed at 0.5°, the precipitate being washed with fresh hexane at 0-5°. Then ethyl iodide (40 ml.) was added and the mixture was refluxed 20 hr. at 100°. The solution was cooled and filtered through florisil; the filtrate was concentrated and the product distilled at 79°/13mm (2 g, 15 mmole, 75% yield). The nmr spectrum (CCl₄) showed signals at 0.8 - 1.2 (3H, two overlapping triplets, -CH₂CH₃), 1.6 - 2.4 (8H, multiplet, includes $\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ singlets at 2.0 ppm and CH₂-CH₃ and 3.4 (1H, triplet,



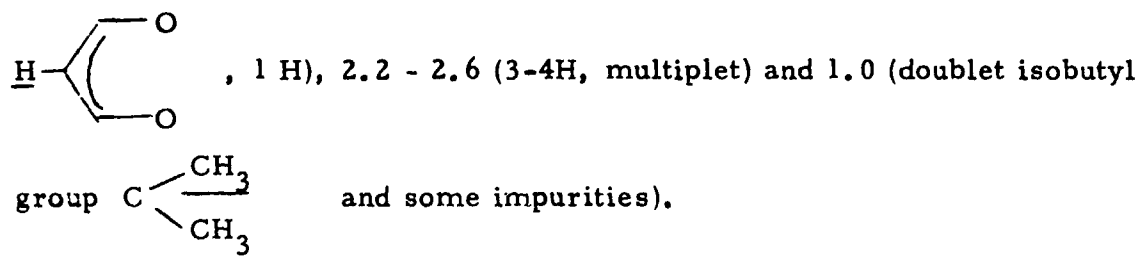
1-Trifluomethylacetylazulene. (5a). To a solution of azulene, (0.54g, 4 mmole) dry carbon tetrachloride 20 ml. under argon at room temperature was added trifluoroacetic acid anhydride (2.2 ml, 15 mmole) after 10 minutes at room temperature 10% sodium bicarbonate solution (10 ml) was added dropwise and the product was isolated by extraction with ether. The crude product was purified by a quick chromatography on silica gel (eluted with benzene). to obtain the title compound (0.98, 3.9 mmole, >99% yield). The solid (m.p. 59-61°, lit 62-63°) had an nmr spectrum (CCl₄) consistent with the desired product, displaying only azulenic aromatic resonance at 6.93-9.7 ppm.

1-acetylazulene. (4) Azulene (0.5g, 3.9 mmole) was added under nitrogen to a mixture of acetic anhydride (8.2 ml, 87 mmole), anhydrous stannic chloride (0.8 ml, 4.1 mmole) and dry methylenechloride (82 ml). After 15 minutes 50 ml 2N hydrochloric acid was added and the organic layer was separated. The aqueous phase was washed with ether and the combined organic extracts were dried (Na_2SO_4), filtered and concentrated to a residual oil. The pure product (0.63 g, 3.7 mmole) was isolated by preparative tlc on silica gel (1:1:ether:hexane). The nmr (CCl_4) spectrum was entirely consistent with the title compound, displaying signals at 2.6 (3H, singlet $\text{az}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$), 6.9-8.3 (6H, multiplet, and 9.5 (1, doublet, $J=6$ cps,



1-methylazulene. (5c) A solution of 1-trifluoromethylazulene (0.92g, 3.8 mmole), water (20 ml) ethanol (20 ml) and sodium hydroxide (24 mmole) was heated at reflux under nitrogen for 2.5 hr. The aqueous phase was acidified (concentrated hydrochloric acid) and extracted with ether. The ether was dried (Na_2SO_4), filtered and concentrated to a residual solid. The solid was taken up in ether (50 ml) and cooled to 0-5°. To this solution was added 14 mmole diazomethane (generated from N-methylnitrosourea, potassium hydroxide and ether at 0-5°). After one hour at 0-5° the solvent was removed at reduced pressure to afford a crystalline residue (710 mg, 3.8 mmole, 100% yield from 1-az- $\overset{\text{O}}{\parallel}{\text{C}}-\text{CF}_3$). The nmr spectrum (CDCl_3) displayed signals at 4.9 (OCH_3 , 3H singlet) and 7-9 (aromatic, 7H, multiplet). Tlc analysis (1:1:ether/hexane) showed one spot at R_f 0.8.

Attempted Condensation of 1-methylazulone with ketones 2-methylnaphthanoate was used as a model for this system. To a mixture of 2-methylnaphthanoate (186 mg., 1 mmole), sodium hydride (2.0 mmole) and THF (4 ml) under nitrogen at 65° was added methylisobutylketone (250 ml, 2.2 mmole) and methanol (15 μ l, catalyst). After 1.5 hours vpc analysis (Se 30, 200°) showed no ester and the mixture was cooled, acidified (dilute HCl) and the product isolated by extraction with ether. The product was purified by preparative tlc (1:1::ether:hexane) to obtain 178 mg (70% yield) of the desired β -diketone. The nmr spectrum (CDCl_3) displayed peaks at 8.4 (1H, singlet), 7-8 (multiplet, 6H), 6.3 (singlet



The above reaction was repeated in DMSO and essentially the same results were obtained.

When the above conditions were tried with 1-methylazulone in THF at 70° with methyl isobutyl ketone, vpc analysis revealed very little reaction. When DMSO was used as a solvent and the reaction conducted at room temperature, the ester was consumed in 20 - 30 minutes. The nmr spectrum of the worked up material showed no diketone chromophores and revealed that the ester function was still intact. The characteristic azulene aromatic pattern was absent (product was only lightly colored) and an isobutyl pattern

was observed. Significantly, vpc analysis of the worked-up mixture showed a quantitative thermal reversion to the starting ester. Thus we have a product that results from the attack of sodium hydride (or the anion of methyl isobutyl ketone) on the azulene nucleus. Thermolysis of such a product would certainly produce a reversion to starting ester. Essentially the same results were found when acetone was substituted for methyl isobutyl ketone.

Attempted Condensation of 1-acetylazulene with Esters. A solution of 1-acetylazulene (42.5mg, 0.25 mmole) in THF (0.5 ml) was added under argon to a solution of methylbenzoate (0.5 mmole), sodium hydride (.6 mmole) THF (0.3 ml) and methanol (5 ml as a catalyst). Vpc analysis showed no ketone after 25 minutes. The mixture was then cooled and methanol (10 drops), aqueous acetic acid (20 drops, 2N.) and ether (10 ml) were successively added.

The ether layer was separated, dried over Na_2SO_4 , filtered and concentrated to a light yellow oil (i. e. no azulene). Vpc analysis showed no 1-acetylazulene and the nmr spectrum showed no 1,3-diketone. Thus we are producing a reactive enolate or observing attack of sodium hydride on the azulene nucleus. A model system using 1-acetylbenzene gives a 70% yield of 1,3-diketone under the above conditions.

The Reaction of 1-acetylazulene with Acetic Anhydride/BF₃. Boron trifluoride was bubbled through acetic acid (100 ml) at 0-5°. Then a solution of 1-acetylazulene (74 mg, 0.45 mmole), acetic anhydride (87 ml, 0.87 mmole) and 1,2-dichloroethane (150 ml) was added at 0 - 5°. The mixture was stirred at 0 - 5° for 0.5 hr. and 12 hr. at room temperature. At this time 1.0 ml 1M sodium acetate solution was added and the mixture was refluxed at 100° for 0.5 hr. The product (52 mg) was isolated by extraction with ether. The nmr spectrum of this product was consistent with 1,3-diacetylazulene. Tlc analysis of this product was identical to that of an authentic sample of 1,3-diacetylazulene.

1-L'methylaminomethylazulene (8). A solution of N,N,N',N' tetramethyldiamino methane (184 mg, 1.8 mmole), paraformaldehyde (47.5 mg, 1.57 mmole) and acetic acid (4 ml) was heated on the steambath to obtain a clear solution. The mixture was cooled and added dropwise to a 0 - 5° solution of azulene (395 mg, 3.08 mmole) and dry methylenechloride (20 ml). After 24 hours at 0 - 5°, 5 percent hydrochloric acid was added and the aqueous phase was washed with 3 x 20 ml methylene chloride. The combined organic extracts were washed once with water and the combined aqueous phases were made basic with 10% NaOH. The amine was isolated by extraction with ether and purified by a quick chromatography on basic alumina (eluted with 90:10::ether:methanol) to obtain the desired product (465 mg, 2.52 mmole) ^{8a}

To 365 mg (1.97 mmole) of the amine in 25 ml ethanol was added 200 μ l (3.2 mmole) methyl iodide at room temperature. After 0.5 hr. the mixture was cooled and the quaternary salt ^{8b} (411 mg, 1.12 mmole) was collected by filtration.

Ethyl 2-acetyl-3 (1-azulyl)propanoate (8c)⁸. Sodium hydride (200 mg, 8.4 mmole) was added to ethylacetoacetate (20 ml, 80.7 mmole) at -78°. To this mixture was added 1-azulylmethyltrimethylammonium Iodide (327 mg, 1 mmole) and the reaction mixture was heated at 80° for one hour. The mixture was cooled and diluted with ether. The ether was exhaustively washed with water; the ether was dried (Na₂SO₄), filtered and concentrated to a residual oil that was chromatographed on silica gel (2:1::ether:hexane) to obtain the pure product (224 mg, 0.83 mmole, 83% purified yield). The nmr spectrum (CDCl₃) displayed signals at 7-8.2 (multiplet, 7H, azulene nucleus), 4-4.4 (quartet, 2H O-CH₂-CH₃, J = 7 cps), 4-3.8 (multiplet, 3H, az-CH₂-CH¹), 2.2 (3H, singlet C⁰-CH₃) and 1.2 (triplet, 3H OCH₂CH₃) ppm.

Suggestions for Future Work

1. The use of enamine and an acid chloride in the synthesis of a 1,3-diazulenylacetylacetone.
2. The use of a less nucleophilic base or a less hindered azuloic acid in the synthesis of a 1,3-diazulenylacetylacetone.
3. The preparation of $\text{az-CH}_2 - \text{C} \begin{array}{l} \nearrow \text{=O} \\ \searrow \text{=O} \end{array}$ for complex formation.

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The Synthesis and Attempted Partial Oxidation of
Stacked Square Planar Iridium Complexes

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Michael R. MacLaury

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Introduction:

Compounds that have chains of stacked metal atoms may be used to examine some interesting electrical phenomena. Krogmann¹ has reported compounds of this type, and we hope to further develop and modify this work. The Krogmann salts exhibit semiconductor behavior along the intermetallic axis, but there are limitations to these compounds. First, these compounds are ionic and are hydrated, thus making the interpretation of the electrical properties difficult. Second, such ionic materials cannot be modified by the incorporation of large polarizable molecules.

The current approach is to prepare three types of molecules. First, we have prepared a series of compounds with ligands that will progressively separate the chains of metal atoms. Although X-ray studies have not been performed, presumably the interchain separation increases as R increases. (figure 1)

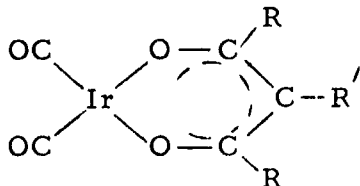


Figure 1

For $R' = H$; $R = CH_3, CH_2CH_3, CH_2CH_2CH_3, CH_2CH(CH_3)_2, C_6H_5$.

For $R' = CH_3$; $R = CH_3$.

Second, work is in progress by L. Libit of this laboratory to modify the basic acetylacetonate ligand by the addition of a dye at either R or R' . The dye chosen is azulene.

Finally, attempts are being made to increase the metal-metal interaction of these stacked compounds by partial oxidation. The model compound for this work, $Ir(CO)_3Cl$, also reported by Krogmann,² is believed to be a mixture of $Ir^I(CO)_3Cl$ and a small amount of $Ir^{II}(CO)_2Cl_2$. Likewise it is hoped that small amounts of an $Ir^{II}(CO)Cl((RCO)_2CR')$ species when introduced into the non-oxidized material will have dramatic effects on both Ir-Ir separation and conductivity properties.

Experimental:⁴

All reactions were carried out under Ar using solvents dried with 4A mc' sieve and deaerated with Ar. In most cases the benzene used was distilled from Na/K under N_2 . Except where noted reagents were used directly from the suppliers with no further purification.

Chlorotricarbonyl iridium(I), $Ir(CO)_3Cl$ (36y, 47w, 47y, 51v)

The $Ir(CO)_3Cl$ used in the following procedures was prepared in the manner of Hieber.⁵ Joan Valentine also described this procedure.³

$IrCl_3 \cdot 3H_2O$ (52.00%) from Matthey Bishop, Inc. was used. The yield in all preparations was never more than 30%.

μ, μ' -dichlorotetrakis(cyclooctene)diiridium(I) $(\text{Ir}(\text{cyclo } \text{C}_8\text{H}_{14})_2\text{Cl})_2$ (10w, 10y, 22y, 49w, 50y)

This compound was prepared in the manner described by Joan Valentine.³ This procedure consistently gave yields of greater than 70%.

μ, μ -dichlorobis(1-5, cyclooctadiene)diiridium(I), $(\text{Ir}(\text{COD})\text{Cl})_2$ (55y)

This procedure followed the method of John Shapley.⁶ 1-5, cyclo-octadiene was purified by filtration through silica gel. $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (5.3g) was dissolved in 180 ml of a deaerated 2:1 ethanol:water solution. Hydroquinone (0.053g) and 5 ml of 1-5, cyclooctadiene were added to the above solution. The solution was heated at reflux under Ar for four hours, after which 50 ml of the solvent was distilled from the reaction solution. The solution was cooled and the red powder was filtered under a stream of Ar. The red powder was washed with ca 50 ml cold methanol, yield 2.54g (49%). The product is stored under Ar.

2,4-Pentanedionatodicarbonyliridium(I), $\text{Ir}(\text{CO})_2(\text{acac})$ (11w, 20w, 21w, 42y, 56w, 56y, 57y)

This compound can be prepared from three different starting materials. Joan Valentine reported that $\text{Ir}(\text{CO})_3\text{Cl}$, NaHCO_3 , and acetylacetone(acac) heated to reflux in benzene for four days, yielded the desired product.³ She also reported that by taking the black precipitate formed by bubbling CO through a hexane solution of $(\text{Ir}(\text{cyclo } \text{C}_8\text{H}_{14})_2\text{Cl})_2$ and heating this black precipitate at reflux with NaHCO_3 and acetylacetone(acac) gives $\text{Ir}(\text{CO})_2(\text{acac})$ in four hours.^{3, 7}

The third procedure starts with Ir(COD)Cl_2 .⁹ Ir(COD)Cl_2 (0.133g) was added to 15 ml of degassed acetone. Na_2CO_3 (0.0979g) and acetylacetone (0.05 ml) were added to the solution, and the mixture was heated at reflux under Ar for one hour. The mixture was cooled and filtered. The solvent was partially removed under reduced pressure, yellow crystals of (COD)Ir(acac) were collected. This compound has been prepared previously.⁹ The (COD)Ir(acac) was redissolved in acetone and CO was bubbled through the solution for about two minutes. The odor of free cyclooctadiene was noted. The solvent was partially removed under reduced pressure and yellow crystals of the product, $\text{Ir(CO)}_2\text{(acac)}$, were collected, yield 0.070g (50%).

In both of the first two methods, a green acetone insoluble product was found. This material absorbs strongly in the infrared (KBr, disc) affording a featureless spectrum over the range $4000\text{-}250\text{ cm}^{-1}$ (42y).

Anal. Found: C, 18.14; H, 1.49; Ir, 59.0. Atom ratios: C(4.93); H(4.80); Ir(1.00). MRM-18.¹⁰

The crude crystals of $\text{Ir(CO)}_2\text{(acac)}$ were further purified by sublimation. (120°C , $<10^{-2}$ torr. The product, $\text{Ir(CO)}_2\text{(acac)}$, formed by all three procedures is identical by ir and prn. Anal. Calc for $\text{Ir(C}_7\text{H}_7\text{O}_4)$: C, 24.21; H, 2.02; Ir, 55.4. Found: C, 23.77; H, 1.94; Ir, 53.9. Atom ratios: C(7.06); H (6.93); Ir(1.00). MRM-7. A dark blue acetone soluble residue remained in the sublimator. The solid state ir of this material showed moderate absorbance throughout the range $4000\text{-}250\text{ cm}^{-1}$. Anal. Found: C, 16.11; H, 1.52; Ir, 55.63. Atom ratios: C, (4.56); H, (5.27); Ir, (1.00) MRM-19. The pmr spectrum in CDCl_3 showed only a singlet at δ 1.5.

3-Methyl, 2, 4-pentanedianotodicarbonyliridium(I), $\text{Ir}(\text{CO})_2(3\text{Me-acac})$

Two procedures can be used to form this compound. The first was reported by Joan Valentine.⁴ $\text{Ir}(\text{CO})_3\text{Cl}$ (0.50 g) prepared by the method of Hieber, 0.5g NaHCO_3 and 0.192g 3-Methyl acetylacetone(3Me-acac) were suspended in 400 ml degassed benzene. The mixture was heated at reflux under Ar for six days. This reaction must be allowed to proceed for more than three days or the yield is very low. The mixture was cooled and filtered to remove NaCl , excess NaHCO_3 , and unreacted $\text{Ir}(\text{CO})_3\text{Cl}$. The flask and filter were rinsed with a small amount of acetone. The solvent was removed under reduced pressure and the residue was dissolved in diethyl ether. The ether solution was transferred to a sublimation apparatus and the solvent was removed by evaporation with a stream of Ar. The product was sublimed (95°C , $<10^{-2}$ torr) to a dry ice/acetone cooled cold finger. The sublimate was recrystallized from ether. The red-orange needles were collected and washed with cold hexane, yield 0.313g (54%). (3lw, 45y, 48y, 53y).

The second procedure takes less time. $\text{Ir}(\text{COD})\text{Cl}_2$ (0.159g) 0.25g Na_2CO_3 , and 0.065g 3-Methyl acetylacetone were added to 15 ml degassed acetone. The mixture was heated at reflux under Ar for one hour. The mixture was cooled and filtered to remove NaCl and excess Na_2CO_3 . CO was bubbled through the filtrate for ca three minutes. A strong odor of cyclooctadiene was noted. The solvent was removed under reduced pressure and the residue was dissolved in diethyl ether. The ether solution was transferred to a sublimation apparatus where the ether was

removed with the aid of a stream of Ar. The product was sublimed (70°C , $<10^{-2}$ torr) to a dry ice/acetone cooled cold finger. The sublimate was recrystallized from diethyl ether. Yield 0.047g (27%). (58w)

The products from these two procedures were found to be identical by ir, pmr, and tlc (1:1 hexane:ether). Anal. Calc for $\text{Ir}(\text{C}_8\text{H}_9\text{O}_4)$: C, 26.58; H, 2.48; Ir, 53.2. Found: C, 26.35; H, 2.44; Ir, 51.86. Atom ratios: C, 8.15; H, 9.05; Ir, 1.00. MRM-11

Dicarbonyl(1,3-diphenylpropan-1,3-dionato)iridium(i), $\text{Ir}(\text{CO})_2((\text{C}_6\text{H}_5\text{CO})_2\text{CH})$

$(\text{Ir}(\text{cycloC}_8\text{H}_{14})_2\text{Cl}_2$ (0.42g) was dissolved in 400 ml petroleum ether (bp 60/90) and CO bubbled through solution until no more black solid precipitated. This black solid was collected on filter paper and washed with hexane to remove cyclooctene. This black material was suspended in 200 ml degassed benzene along with ca 0.5g NaHCO_3 . To this mixture was added 0.235g dibenzoylmethane.¹¹ The mixture was heated at reflux under Ar for 24 hours. This reaction must be allowed to proceed for more than two hours or the yield is very low. The mixture was cooled and filtered to remove NaCl, excess NaHCO_3 , and unreacted black starting material. The flask and filter were washed with a small amount of acetone. The solvent was removed under reduced pressure and the residue was transferred to a sublimator. The product was sublimed (140°C 10^{-2} torr) to a dry ice/acetone-cooled cold finger. The sublimate was crystallized from acetone, yield 0.226g (51%). (13 w, 52y, 53w, 55w).

Recrystallizations at different times have produced two crystal forms. The most common crystals are red needles, but twice thin gold metallic flakes have been obtained (37y). The melting point of the red form is 183°C and that of the gold form is 195°C. Both forms give identical analysis. Anal. Red form: Calc for $\text{Ir}(\text{C}_{17}\text{H}_{11}\text{O}_4)$: C, 43.29; H, 2.34; Ir, 40.75. Found: C, 43.29; H, 2.43; Ir, 40.83. Atom ratios: C, 17.0; H, 11.4; Ir, 1.00. MRM-16. Anal. Gold form: Found: C, 43.14; H, 2.40; Ir, 40.54. Atom ratios: C, 17.1; H, 11.4; Ir, 1.00. MRM-17

3,5-Heptanedionatodicarbonyliridium(I), $\text{Ir}(\text{CO})_2((\text{CH}_3\text{CH}_2\text{CO})_2\text{CH})$

Black material from $\text{Ir}(\text{cycloC}_8\text{H}_{14})_2\text{Cl}_2$ and CO (0.53g), 0.28g NaHCO_3 , and 0.22ml 3,5-heptanedione¹¹ were suspended in degassed benzene. The mixture was heated at reflux under Ar for 22 hours. The mixture was cooled and filtered. The flask and filter were washed with a small amount of diethyl ether. The solvent was removed under reduced pressure and the residue dissolved in acetone. The product was obtained by cooling the acetone solution to -78°C with dry ice. Long green-gold needles were collected. (8y, 9w, 9y, 11y). The melting point of the product is 89°C. Anal. Calc for $\text{Ir}(\text{C}_9\text{H}_{11}\text{O}_4)$: C, 28.90; H, 2.94. Found: C, 27.90; H, 2.80. MRM-15

4,6-Nonanedionedicarbonyliridium(I), $\text{Ir}(\text{CO})_2((\text{CH}_3\text{CH}_2\text{CH}_2\text{CO})_2\text{CH})$

Black material from $\text{Ir}(\text{cycloC}_8\text{H}_{14})_2\text{Cl}_2$ and CO (0.78g), 0.72g NaHCO_3 , and 0.42g 4,6-nonanedione¹¹ were suspended in 200 ml degassed benzene. The mixture was heated at reflux with Ar for five hours. The mixture was cooled and filtered. The flask and filter were washed with a

small amount of acetone. The solvent was removed under reduced pressure and the residue was transferred to a sublimator. The impure product was sublimed (85°C , $< 10^{-1}$ torr) to a dry ice/acetone-cooled cold finger.

The oily sublimate was washed from the probe with acetone. Metallic green crystals formed only at -78°C . At higher temperatures the crystals became a red oil. Thin film ir of the red oil showed the presence of excess 4,6-nonanedione. (12w, 12y)

Ethyl 3-Oxobutanoatedicarbonyliridium(I), $\text{Ir}(\text{CO})_2(\text{CH}_3\text{CH}_2\text{OCOCHCOCH}_3)$

$\text{Ir}(\text{CO})_3\text{Cl}$ (0.075g), ca 0.1g NaHCO_3 , and 0.057g ethyl 3 oxobutanoate were suspended in 50 ml degassed benzene. The mixture was heated at reflux under Ar for four days, and then cooled and filtered. The solvent was removed under reduced pressure and gold crystals were collected.

The product can be recrystallized from hexane by cooling to -78°C .

Yield 0.037g (41%). Anal. Calc for $\text{Ir}(\text{C}_8\text{H}_9\text{O}_5)$: C, 25.49; H, 2.39; Ir, 51.1. Found: C, 24.44; H, 2.33; Ir, 49.12. Atom ratios: C, 7.98; H, 9.12; Ir, 1.00. MRM-20. (50w, 51w)

Attempted preparation of 3-chloroacetylacetonedicarbonyliridium(I),

$\text{Ir}(\text{CO})_2(3\text{-Cl-acac})$

3-chloroacetylacetone was prepared by the action of SO_2Cl_2 on acetylacetone.¹² 67.5 g SO_2Cl_2 was slowly added to 50 g acetylacetone cooled in an ice bath. The solution was stirred for two hours until glpc indicated the complete absence of acetylacetone. 100 ml water was added and the product was extracted into diethyl ether. The ether was removed under reduced pressure and the product purified by vacuum distillation (water aspirator, 67°C). (36w)

$\text{Ir}(\text{CO})_3\text{Cl}$ (0.124 g), 0.151g NaHCO_3 , and 0.118g 3 Cl-acac were added to degassed benzene. The mixture was heated at reflux under Ar for four days, then cooled and filtered. The filtrate is deep red. The solvent was removed under reduced pressure. Adsorption of the residue was dissolved in CDCl_3 and pmr spectrum was taken. The spectrum showed free 3 Cl-acac δ 2.2 and product δ 1.4. Attempts to isolate pure product were not successful. (35y, 37w, 38w, 38y)

Attempted Preparation of 1-Dimethylaminomethylazulenedicarbonylchloro-iridium(I), $\text{Ir}(\text{CO})_2(\text{N}(\text{CH}_3)_2\text{CH}_2\text{C}_{10}\text{H}_{10})\text{Cl}$

$\text{Ir}(\text{CO})_3\text{Cl}$ (0.162g) ca .2g NaHCO_3 , and 0.09 g 1-dimethylaminomethylazulene¹¹ were suspended in degassed benzene. The mixture was heated at reflux under Ar for one hour. At this time all of the $\text{Ir}(\text{CO})_3\text{Cl}$ had gone into solution and the color of the solution had changed from deep blue (color of ligand) to dark red. The solution was cooled and filtered. The solvent was removed under reduced pressure. Solution (CHCl_3) ir indicated Ir-CO stretches at 2060 and 1980 cm^{-1} . Attempted purification by sublimation destroyed the compound. (49y, 52w)

Attempted Preparation of Ethyl 2-acetyl-3-(1-azulyl)propanoatedicarbonyl-iridium(I), $\text{Ir}(\text{CO})_2(\text{CH}_3\text{CH}_2\text{OCO}(\text{CCH}_2\text{C}_{10}\text{H}_{10})\text{COCH}_3)$

All attempts to form this compound have failed. In all cases the azulene ligand¹¹ was recovered from the reaction mixture and no indication of an iridium complex was noted.

Standard conditions were tried. $\text{Ir}(\text{CO})_3\text{Cl}$, NaHCO_3 , and ligand were suspended in benzene, and the mixture was heated at reflux for two

days. Preparative tlc recovered 81% of the ligand (silica gel, 1:1 hexane:ether). (54y)

A soluble base, tri-n-butyl amine, instead of NaHCO_3 , $\text{Ir}(\text{CO})_3\text{Cl}$, and ligand were heated under reflux in benzene for 15 hours. Preparative tlc recovered 45% of the ligand (57w).

Treatment of $(\text{Ir}(\text{COD})\text{Cl})_2$ and Na_2CO_3 with the ligand in acetone for 16 hours yielded no complex. Preparative tlc recovered 45% of the ligand. (59 w)

The ligand was treated with NaH in benzene to form the anion. $\text{Ir}(\text{CO})_3\text{Cl}$ was added after the formation of the anion, and the mixture was heated at reflux under Ar for five days. Workup of the reaction by preparative tlc yielded three bands. One was identified as the starting ligand (34%), another appeared, by pmr, to be ethyl-3-oxobutanoate, and the third was the black residue that remained at the origin of the tlc plate. When this reaction was repeated and allowed to heat at reflux for only one day, 56% of the ligand was recovered by preparative tlc. (59y, 63w)

The ligand was treated with NaH in tetrahydrofuran(THF) to form the anion. $\text{Ir}(\text{CO})_3\text{Cl}$ was added and the mixture was heated under reflux and Ar for two days. Tlc showed only the presence of free ligand. (64 y)

$\text{Ir}(\text{CO})_3\text{Cl}$ treated with tri-ethylamine

$\text{Ir}(\text{CO})_3\text{Cl}$ was suspended in degassed benzene, and a small amount of tri-ethylamine was added. The mixture was capped under Ar and stirred at room temperature for ten hours. After ten hours all of the $\text{Ir}(\text{CO})_3\text{Cl}$ was dissolved and the solution was light brown in color. Tlc indicated only

tri-ethylamine. No color change or precipitate was observed when CO was bubbled through the solution. The solvent was removed under reduced pressure. The brown oily residue is not soluble in diethyl ether but it is soluble in acetone. A pmr in acetone- d_6 shows that no complex was formed with triethylamine. (62y)

Attempted partial oxidation by chlorination

All chlorination using chlorine was done either in benzene, which was distilled from Na/K, or carbon tetrachloride, which was dried over activated 4A mol sieve. The Critical Tables III pp. 261 give solubility data for Cl_2 in CCl_4 (2.32×10^{-3} moles Cl_2 /ml CCl_4 saturated at room temperature). (28y) The Stanford Analytical Lab has measured the concentration of Cl_2 in a benzene saturated solution at room temperature. Anal. Cl, 8.60 and 8.66. (2.14×10^{-3} moles Cl_2 /ml C_6H_6) MRM-1. (28w) Knowing these two values, chlorination can be done quantitatively. All reactions were done under an atmosphere of Ar.

Chlorination of $Ir(CO)_2(acac)$

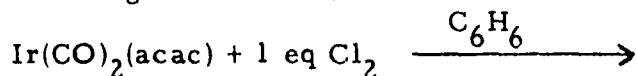
A known amount of $Ir(CO)_2(acac)$ was dissolved in CCl_4 in a pmr tube. Upon standing the color changed from light yellow to red, with a dark flocculant precipitate. Pmr showed two singlets at δ 2.2 and δ 5.8 in the ratio of ca 6:1. Addition of one mole equivalent Cl_2 to the pmr tube caused the solution to change to yellow and a new singlet was observed at δ 2.5. The area of this new peak is exactly accounted for by the decrease in area of the original peak at δ 2.2. Addition of excess Cl_2 caused both of the original peaks to disappear. (21y, 28y)

A similar experiment using benzene was performed. The pmr showed two singlets at δ 1.5 and δ 5.1. No color change is noted over long periods of time, the solution remains pale yellow for a period of days. The addition of one mole equivalent Cl_2 causes the singlet at δ 5.1 to disappear and the singlet at δ 1.5 is broadened, but no new peaks were observed. (28w, 29y) The addition of Cl_2 causes the color to change dramatically from pale yellow to deep red. (28w, 29y)

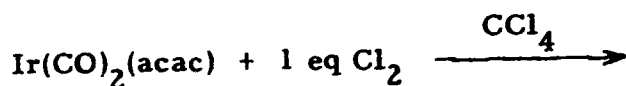
When the chlorination in benzene was followed by tlc (1:1 hexane: ether) until no starting $\text{Ir}(\text{CO})_2(\text{acac})$ was detectable, the solution ir showed four sharp absorptions in the Ir-CO region; 2150, 2130, 2100, 2080 cm^{-1} . (56y)

$\text{Ir}(\text{CO})_2(\text{acac})$ was dissolved in dichloromethane and a large excess Cl_2 was added. The solvent was removed under reduced pressure. The light yellow powder turned red-brown and oily when exposed to air (probably moisture). The CHCl_3 solution ir of this yellow powder showed Ir-CO absorbance at 2150 and 2100 cm^{-1} . (14w) The red-brown product exhibits broad absorbance throughout the ir range ($4000\text{-}250 \text{ cm}^{-1}$). (14y, 19y)

Attempts to obtain analysis of any of the above reaction products have yielded ambiguous results.



Anal. Found: C, 21.33; H, 1.48; Cl, 7.17. Atom ratio: C, 8.9; H, 7.4; Cl, 1.00 MRM-2. Anal. Found: c, 23.14; H, 1.82; Cl, 10.58. Atom ratio: C, 6.45; H, 6.1; Cl, 1.00 MRM-9.



Anal. Found: C, 16.73; H, 1.22; Cl, 25.67 Atom ratio: C, 1.92; H, 1.68;

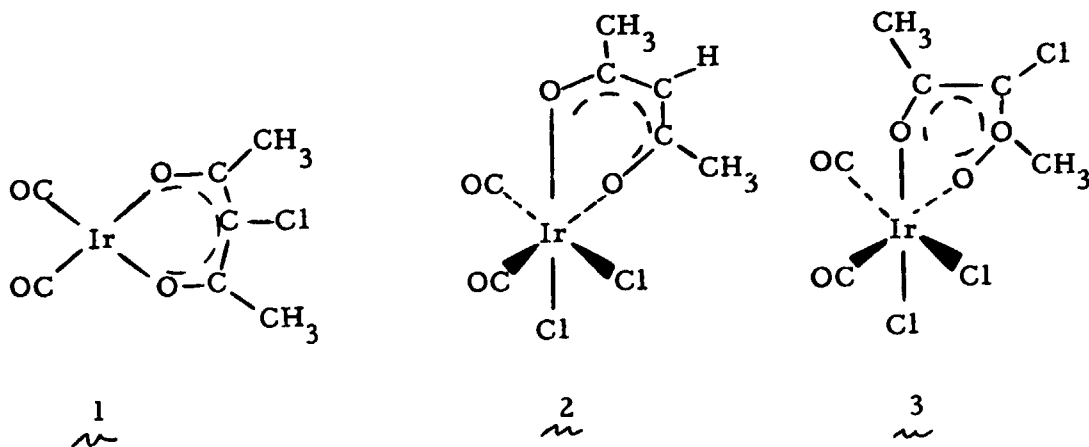
Cl, 1.00. MRM-4 Anal. Found: C, 17.34; H, 1.27; Cl, 25.84

Atom ratio: C, 2.00; H, 1.75; Cl, 1.00 MRM-8

1. Calc for $\text{Ir}(\text{C}_7\text{H}_6\text{O}_4\text{Cl})$: C, 22.01; H, 1.57; Cl, 9.40; Ir, 50.95.

2. Calc for $\text{Ir}(\text{C}_7\text{H}_7\text{O}_4\text{Cl}_2)$: C, 20.1; H, 1.67; Cl, 16.9; Ir, 46.0.

3. Calc for $\text{Ir}(\text{C}_7\text{H}_6\text{O}_4\text{Cl}_3)$: C, 18.6; H, 1.33; Cl, 23.55; Ir, 42.5.



geometry not determined

Chlorination of $\text{Ir}(\text{CO})_2(3\text{Me-acac})$

A known amount of $\text{Ir}(\text{CO})_2(3\text{Me-acac})$ was dissolved in C_6D_6 in a pmr tube. Two singlet peaks were observed at δ 1.3 and δ 1.7 in the ratio of ca 1:2. After addition of one-half mole equivalent of Cl_2 , a marked decrease and broadening of the original peaks was observed. (44w)

A dark flocculant precipitate was also formed. The addition of up to four mole equivalents of Cl_2 did not change the spectrum. Free 3-methylacetylacetone has been observed when the chlorination was followed with tlc

(1:1 hexane:ether), (60y) The color changes were marked. The starting solution is pale yellow, then upon addition of a small amount of Cl_2 the color was observed to change to deep orange to red olive green to bright yellow. The bright yellow stage was formed by large amounts of Cl_2 . (60w) The intermediate and final stages were found to be water sensitive, in that additions of moist Ar caused a dark flocculant precipitate to form. (60y) The nujol ir of this precipitate showed broad absorbance in the region $2100\text{-}2000\text{ cm}^{-1}$ and overall strong absorbance for the whole ir range ($4000\text{-}250\text{ cm}^{-1}$). The benzene solution of the deep yellow filtrate showed strong featureless absorbance except for peaks at 2140, 2095, 535, and 505 cm^{-1} . The addition of a large amount Cl_2 caused the dark precipitate to go into solution. The tlc of the resultant deep yellow solution shows a new compound and no free 3-methyl acetylacetone. The benzene solution ir of this material showed the same Ir-CO stretches as above (2140 and 2095 cm^{-1}) but in addition there were many new sharp bands in the "finger-print" region ($1300\text{-}400\text{ cm}^{-1}$). These new bands do not correspond to either starting material or free 3-methyl acetylacetone. (60w) A portion of the dark precipitate was washed with THF, suspended in benzene and treated with enough Cl_2 to partially dissolve it. The solution was filtered and the solvent was removed from the filtrate under reduced pressure. The solid-state ir was taken in KBr. Although the pellet was clear yellow the sample absorbed completely throughout the ir region ($4000\text{-}250\text{ cm}^{-1}$). (60y)

A reaction was observed between carbontetrachloride and $\text{Ir}(\text{CO})_2(3\text{Me-acac})$. When $\text{Ir}(\text{CO})_2(3\text{Me-acac})$ was dissolved in CCl_4 the color

changed from pale yellow to red in a period of several minutes. Tlc showed no remaining starting compound. Upon standing for one hour the solution changed from red to yellow. Solution ir showed two new sharp bands at 2150 and 2100 cm^{-1} . Pmr showed four peaks δ 2.3, δ 2.1, δ 1.0, and δ 0.8 in the ratio of 3:2:1:3. The CCl_4 was removed under reduced pressure affording a yellow oil. This oil was dissolved in benzene and added to an equal amount of $\text{Ir}(\text{CO})_2(3\text{Me-acac})$ also dissolved in benzene.

Upon addition of the bright yellow solution of the CCl_4 treated $\text{Ir}(\text{CO})_2(3\text{Me-acac})$ to the pale yellow solution of the untreated starting compound, the color changed to deep red. Tlc showed starting compound and non-moving component that is characteristic of the CCl_4 treated material. The solution ir (benzene) of this red solution showed Ir-CO stretches from both materials (2150, 2100, and 2065, 1990 cm^{-1}). The solvent was removed under reduced pressure and the residue redissolved in C_6D_6 . A pmr was obtained (δ 1.75, δ 1.70, δ 1.55, δ 1.3, δ 1.25 in the ratio of 3:3:2:3:2). Solution ir indicated that the original mixture had been changed during the evaporation process. The ir now showed Ir-CO peaks at 2280, 2150, 2100, 2060, cm^{-1} . (37y, 40y, 65y, 66w).

A single experiment using N-chlorosuccinimide(NCS) as the chlorinating reagent was performed. An equal mole quantity of NCS was added to $\text{Ir}(\text{CO})_2(3\text{Me-acac})$ in a pmr tube using C_6D_6 as solvent. The color changed from pale yellow to orange yellow. Six new peaks were observed that could not be identified as either starting material, NCS, or succinimide. No further work has been done using NCS. (46y)

Gaseous Cl_2 was passed over crystals of $\text{Ir}(\text{CO})_2(3\text{Me-acac})$. The crystals became "sticky" and changed color to dark red. Solid state ir(KBr) showed Ir-CO bands at 2150, 2100, and 2060 cm^{-1} . This material became very dark when exposed to moisture. (61w). The material dissolved in benzene and appeared to react with THF to afford a dark flocculent precipitate and a yellow solution. Solid state ir (KBr) of these solvent-treated materials were strongly absorbing and featureless, with only a slight hint that some of the original compound was intact. (62w) Sublimation of the "sticky" red solid (110°C , 10^{-2} torr) afforded two materials. The sublimate, a dark green solid, was soluble in either acetone or CDCl_3 . Both solutions were ruby red. Pmr in CDCl_3 showed the two starting peaks and the two new peaks (δ 2.3, δ 2.2, δ 2.0, δ 1.8 in the ratio of 1:7.5:4:1). The solid state ir(KBr) showed a broad, featureless, moderately absorbing spectrum. Anal. Found: C, 24.59; H, 2.42; Cl, 6.15; Ir, 43.25. Atom ratios: C, 9.11; H, 11.70; Cl, 0.77; Ir, 1.00; O (by difference), 7.15. MRM-21 The residue that remains after sublimation was acetone soluble to give a brown green solution. Pmr in acetone- d_6 failed to show any protons. The solid state ir(KBr) showed strong absorbance over the whole range ($4000\text{-}250\text{ cm}^{-1}$). Anal. Found: C, 11.72; H, 0.93; Cl, 19.44; Ir, 50.43. Atom ratio: C, 3.73; H, 3.55; Cl, 2.09; Ir, 1.00; O (by difference), 4.19. MRM-22 (62w, 63y, 64w)

Discussion:

It is evident from the variety of synthetic procedures used to prepare the $\text{Ir}(\text{CO})_2(\text{R}(\text{CO})\text{R}'\text{C}(\text{CO})\text{R}'')$ that have been described, that no general approach has been found. Substitution at the central carbon ($\text{R}'\text{H}$) seems to limit ready formation of the metal complex. These ligands, 3Me-acac and ethyl 2-acetyl-3-(1-azulyl) propanoate, do not enolize as the unsubstituted ligands do.

It has been thought that the black material obtained by bubbling CO through a solution of $(\text{Ir}(\text{cycloC}_8\text{H}_{14})_2\text{Cl})_2$ was the same as $\text{Ir}(\text{CO})_3\text{Cl}$ obtained by the Hieber procedure.⁷ But these two materials do not, in all cases, substitute for each other in reactions. For example the black material does not react with 3-methylacetylacetone as does $\text{Ir}(\text{CO})_3\text{Cl}$.

At least two different reactions appear to be taking place during the chlorination reactions. First the Ir(I) is being oxidized to Ir(III). This is established by comparison of the ir Ir-CO stretches of these compounds with the ir Ir-CO stretches of Ir(III) compounds reported by Malatesta.¹³ The second apparent reaction is the chlorination of the acetylacetone ligand. Carbon tetrachloride seems only to oxidize the Ir and does not chlorinate the ligand. Similar attempts by other workers to use Cl_2 met with failure and it may be that Cl_2 is too strong an oxidizing agent.¹⁴ Further work is intended to determine the most suitable method of preparing the partially oxidized materials. From past experience one can predict that these substances will probably be oxygen, water-and heat-sensitive.

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IV. EXPERIMENTAL PROGRAM

Physical Measurements - G. Wrighton

In order to meet the needs of determining relevant properties of our special materials, several new types of measurement have been made along with continuing work on the type of measurements described in earlier reports.

To investigate the superconducting transition temperatures of some intercalated compounds being prepared by Drs. Winkler and Mayer, a device for monitoring the diamagnetic susceptibility at low temperature was built. The device consisted of a coil installed at the bottom of a Helium Dewar. The coil formed the tank circuit of an LC oscillator, tuned to approximately 1.78Mhz. By monitoring the change in frequency from the norm the superconducting transition can be examined. The temperature can be varied from 4.2°K to 1.35°K by pumping on the Helium bath. The system is designed such that samples can be interchanged at the lowest temperature. This facilitates measurements on a large number of samples in a short time.

A typical curve of a test compound is shown in Fig. 1. Several intercalated compounds have been studied and this work is continuing.

A number of one-dimensional (1.D) compounds were checked for superconductivity at low temperature. These are listed in Table I. None of the compounds were found to be superconducting down to 1.4°K.

Recent measurements by Kuse and Zeller (Phys. Rev. Letters 27, 1060 (1971)) on $K_2Pt(CN)_4Br_{0.3} \cdot 2.3H_2O$ suggest that reflectance measurements in the visible and uv would be useful in clarifying the properties of the one dimensional compounds. To this end a simple device which fits in to the DK-2 spectrometer was built. A mirror reflects the beam onto a pellet of the sample which reflects via another mirror back into the spectrometer.

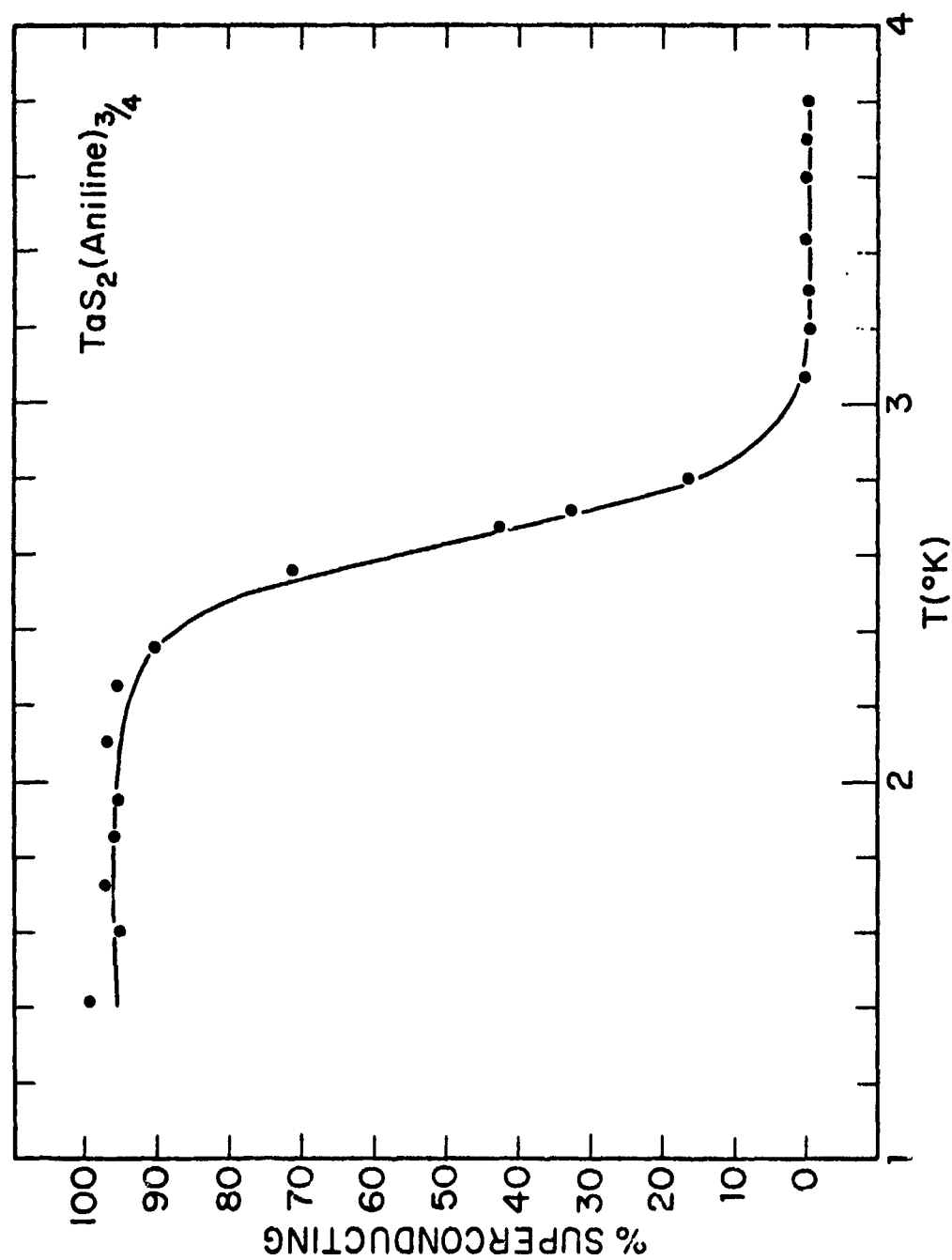


Fig. 1 Superconducting Transition of $\text{TaS}_2(\text{Aniline})_{3/4}$

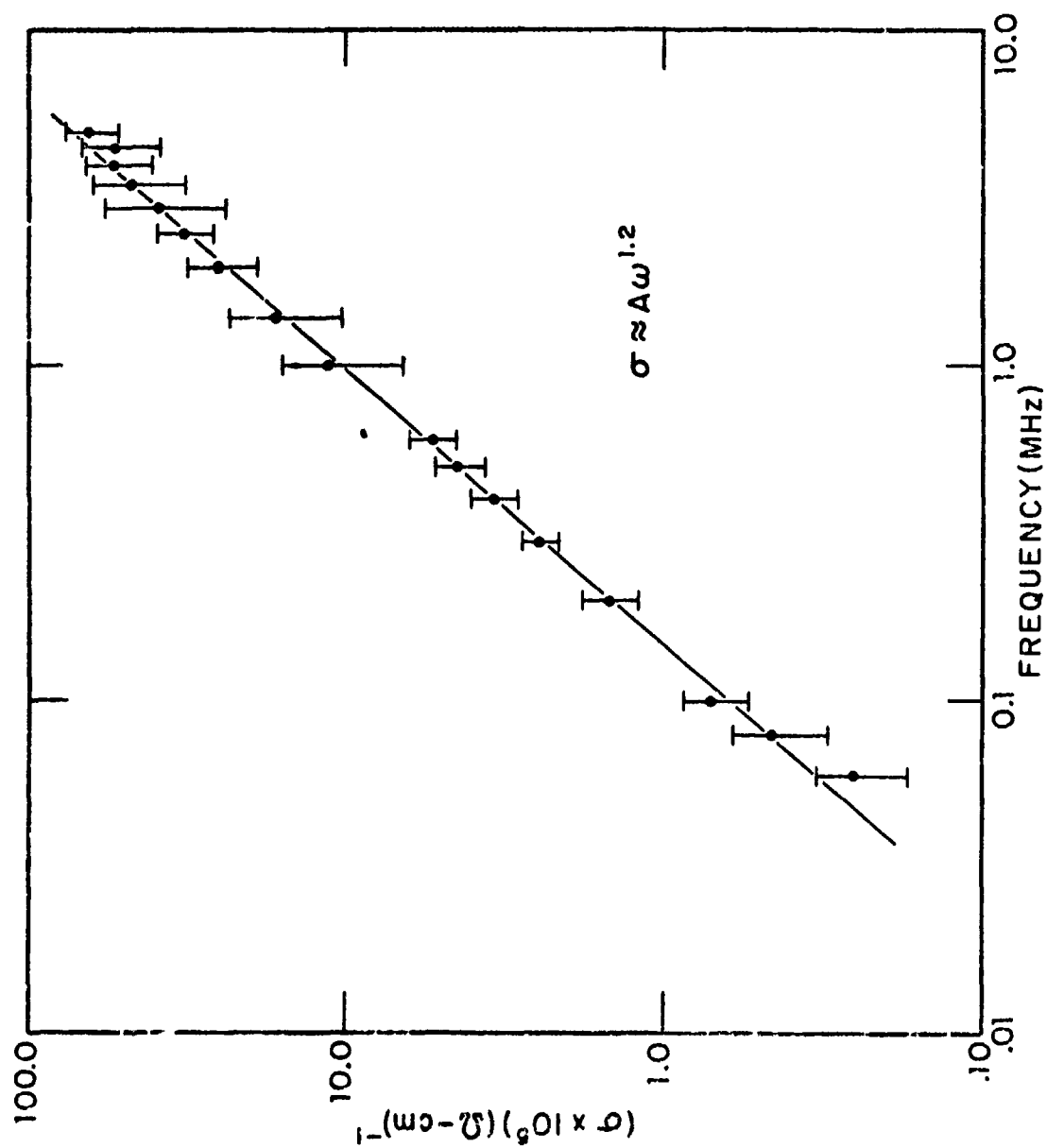


Fig. 2 Frequency Dependence of Conductivity of $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}\times 2.3\text{H}_2\text{O}$ at Room Temperature

The results on $K_2Pt(CN)_4Br_{0.3} \cdot 2.3H_2O$ are in agreement with the results of Kuse and Zeller. This reflectance and other spectrometric work is continuing.

As discussed earlier, the conduction mechanism in the 1.D compounds is governed by a hopping process (See Bloch, Weisman, and Varma). This is based on the apparent $1/T^{1/2}$ dependence of $\ln \sigma$. This hopping process should also manifest itself in the ac conduction properties. Pollack and Geballe (Phys. Rev. 122, 1742 (1961)) show that in silicon the hopping process leads to an ac conductance $\sigma = A\omega^s$ where $s \approx .8$. The ac conductance of $K_2Pt(CN)_4Br_{0.3} \cdot 2.3H_2O$ as a function of frequency at room temperature is shown in Fig. 2. This result helps confirm the hopping type conduction process discussed earlier. Also measurement of the temperature dependence of the dielectric constant on other 1.D compounds tend to support this hypothesis.

Table I

Linear Compounds not Superconducting at 1.4°K

1. $K_{1.8}Pt(C_2O_4)_2 \cdot 2H_2O$
2. 1,1' Diethyl (2,2') Cyanine + $(TCNQ)_2^-$
3. $Ir(CO)_2$ tropolone
4. $Rh(CO)_2Cl_2$
5. $K_2Pt(CN)_4Br_{0.3} \cdot 2.3H_2O$
6. $Ir(CO)_{2.9}Cl_{1.1}$
7. $Ni(DMG)_2I_2$

Specific Heat Measurements - S. Spence

Work is continuing on the apparatus for automatic measurement of the specific heat of specimens in the temperature range from 4K to 400K.

Computer Modeling Facility - C. Berney, F. DeFrancesco, W. A. Little

The computer modeling facility built under NASA Contract # JPL 952944 now is in use as an aid to planning the synthesis of Krogmann-like salts. Much of the software for molecular manipulations has been completed. Certain strain relief and utility routines for extracting data from the display remain to be written. Several Krogmann salts and dye-metal complexes are now in memory and available on the display. Others are being added.

Electron-optical Light Pipe - W. A. Little

As an outgrowth of discussions of a classical, mechanistic model of a superconductor, a new type of effective force on a charged particle moving in a time-dependent, spatially inhomogeneous field has been recognized. This has suggested a number of novel electronic and solid state devices. One has been built and demonstrated. This is a device which is an electron optical analogue to an optical light pipe. A paper on this is to be published in the Journal of Applied Physics. A patent disclosure has been filed on this and related devices.

Transport in Linear Transition Metal Compounds - R. Bube, J. McKenzie, C. Wu

Electrical conductivity as a function of temperature and atmosphere has been investigated for several of the compounds of interest. Additional insight into the nature of the transport processes has been gained from measurements of thermoelectric power.

Results of this work are summarized in a draft copy of a paper, "Thermoelectric Analysis of Transport in Linear Transition Metal Organo-Metallic Compounds," which is enclosed, and which is to be submitted for publication in Applied Physics Letters.

THERMOELECTRIC ANALYSIS OF TRANSPORT IN
LINEAR TRANSITION METAL ORGANO-METALLIC COMPOUNDS*

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ABSTRACT

Thermoelectric analysis of the conductivity in $\text{Ir}(\text{CO}_3)\text{Br}$ and $\text{K}_2\text{Pt}(\text{CN})_4\text{Cl}_{0.3} \cdot x \text{H}_2\text{O}$ as a function of temperature and atmosphere gives additional insight into the transport processes involved. The temperature independence of the thermoelectric power indicates that the observed temperature dependence of conductivity is due to the mobility of the carriers, and is consistent with a hopping model for conductivity. Two quite different electronic states of $\text{K}_2\text{Pt}(\text{CN})_4\text{Cl}_{0.3} \cdot x \text{H}_2\text{O}$ are defined: (1) a high-conductivity hydrated state with $x \approx 2.6$, which exhibits a small positive thermoelectric power, and (2) a lower-conductivity dehydrated state with $x \approx 0$, which exhibits a larger negative thermoelectric power.

* Research sponsored by the Advanced Research Projects Agency through the Office of Naval Research, and by the National Science Foundation (C.W.).

INTRODUCTION

Considerable interest has developed in linear transition metal organo-metallic compounds of the Krogmann-compound family.¹ In such materials the possibility of metallic conductivity along the transition-metal chains has been suggested, along with the proposal that these materials be viewed as prototype systems for high-temperature superconductors.² Appreciable uncertainty exists about the actual transport properties of these and possibly related materials. Kuse and Zeller³ measured the optical reflectivity of $K_2P^{+}(CN)_4Br_{0.3} \cdot x H_2O$ and concluded that they had detected the plasma absorption edge of free carriers with light polarized parallel to the metal chains. Since they also observed a strongly temperature-dependent electrical conductivity (14 orders of magnitude between 20° and 300°K), they attributed this dependence to the mobility of free carriers hindered by interrupted metallic chains. Bloch et al.⁴ argue against this interpretation of the optical data, and show that the \ln conductivity varies as $1/T^{1/2}$, as predicted for conductivity due to hopping between disordered localized states.^{5,6} Since the temperature dependence of conductivity is the same for such materials as NMP-TCNQ, Bloch et al.⁴ argue for a similar hopping process due to disorder in these materials. Epstein et al.⁷ on the other hand offer a variety of electrical and magnetic evidence for the reality of a metal-insulator transition in NMP-TCNQ at 200°K.

Although Kuse and Zeller indicate no difficulty with dehydration of their material, and argue that their attempts to identify ionic conductivity are negative, measurements by Rupp⁸ on the same material indicate marked changes in NMR characteristics upon dehydration, as evidenced by the disappearance of a Knight-shift upon dehydration.

In order to investigate the transport properties by a different

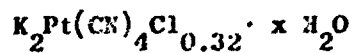
technique, we have measured thermoelectric power of two of these materials: $\text{Ir}(\text{CO}_3)\text{Br}$, which has no hydration and shows no sensitivity to changes in atmosphere, and $\text{K}_2\text{Pt}(\text{CN})_4\text{Cl}_{0.3} \cdot x\text{H}_2\text{O}$, which we were able to measure in both hydrated and dehydrated states.

$\text{Ir}(\text{CO}_3)\text{Br}$

Four-point measurements of electrical conductivity indicate that the 300°K conductivity in $\text{Ir}(\text{CO}_3)\text{Br}$ parallel to the Ir chains is of the order of $3 \times 10^{-4} (\text{ohm-cm})^{-1}$ in either a "wet" or "dry" atmosphere. In this material the Ir-Ir distance is 2.85Å, as compared to 2.71Å in Ir metal. Thermoelectric power measurements at 300°K are well behaved and give a value of + 440 microV/°K.

Results of measurement of electrical conductivity and thermoelectric power as a function of temperature between 230° and 320°K are given in Figure 1. The thermoelectric power is essentially temperature independent, indicating that the observed temperature dependence of conductivity is due to the mobility. If the thermoelectric power is analyzed in terms of a semiconductor model, the values of carrier density and mobility indicated in the lower portion of Figure 1 are obtained. The hole density is calculated to be of the order of $3 \times 10^{17} \text{ cm}^{-3}$ and the hole mobility has an effective activation energy of about 0.18 eV. The magnitude of the mobility is too small by the extent of the approximation that uses the geometric cross section of the crystal to calculate the conductivity.

These results indicate that hole transport in this material is by a hopping process, and that thermal excitation of free holes does not contribute significantly to the hole density, at least over the measured temperature range.



Measured values of the electrical conductivity of $\text{K}_2\text{Pt}(\text{CN})_4\text{Cl}_{0.32} \cdot x \text{H}_2\text{O}$ vary significantly from sample to sample and with changes in the relative humidity of the atmosphere. Four-point measurements in the "wet" state ($x \approx 1.6$) vary from 1 to $10^2 \text{ (ohm-cm)}^{-1}$ at 300°K for the conductivity parallel to the Pt chains. In this material the Pt-Pt spacing is 2.88Å, as compared to 2.76Å in Pt metal. The conductivity in the transverse direction, for which only two-point measurements have been possible to date, is about 10^{-2} to 10^{-3} that of the parallel conductivity. Both parallel and transverse conductivity decrease by three or more orders of magnitude when the crystal is brought from a "wet" state to a "dry" state in a dry gas or in vacuum.

The variation of four-point parallel conductivity with atmosphere is shown in Figure 2 for a crystal with initial "wet" conductivity of 14 (ohm-cm)^{-1} . Attempts to reverse the process by exposing a "dry" crystal to a humid atmosphere are partially but not completely effective.

Measurements of thermoelectric power in "wet" and "dry" states reveal that the sign of the thermoelectric power is changed by the dehydration process. Figure 3a shows curves of thermoelectric voltage vs. temperature difference for five temperatures between 278° and 331°K. In the "wet" state, the thermoelectric power is of the order of + 15 microV/°K, but upon heating above room temperature, the crystal reverts spontaneously to the "dry" state with thermoelectric power of - 93 microV/°K. The thermoelectric power vs. temperature difference curves in the two states at 300°K are shown in Figure 3b.

The temperature dependence of conductivity in the "wet" state, as preserved by protecting the crystal by oil, and in the "dry" state, are compared in Figure 4 with data given by Kuse and Zeller³ for the related Br-containing compound. Linear dependence is observed between \ln conductivity and $1/T^{1/2}$ for our data over the measured range.

This work was carried out as part of an interdisciplinary program with Prof. J. P. Collman of Chemistry and Prof. W. A. Little of Physics at Stanford. In addition we are indebted to Dr. Dorin Lin and Dr. Tammo Winkler for the preparation of the crystals used.

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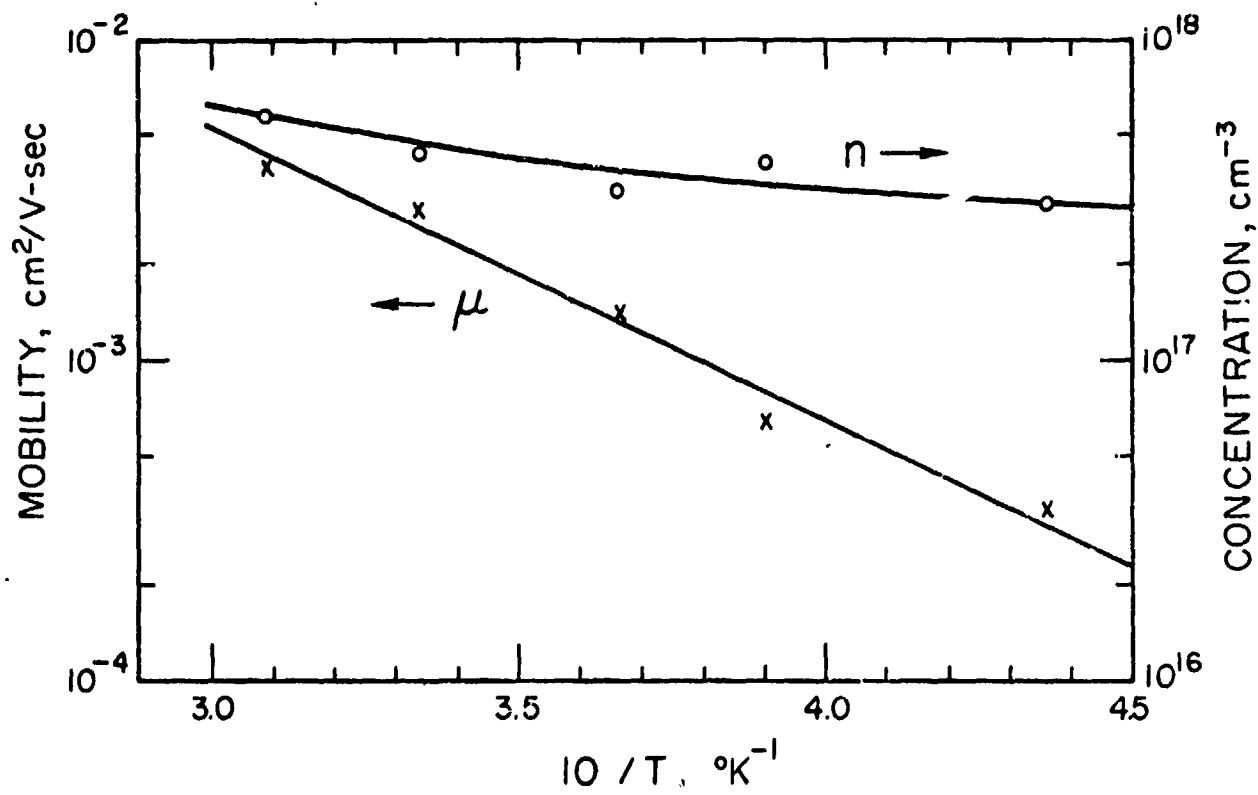
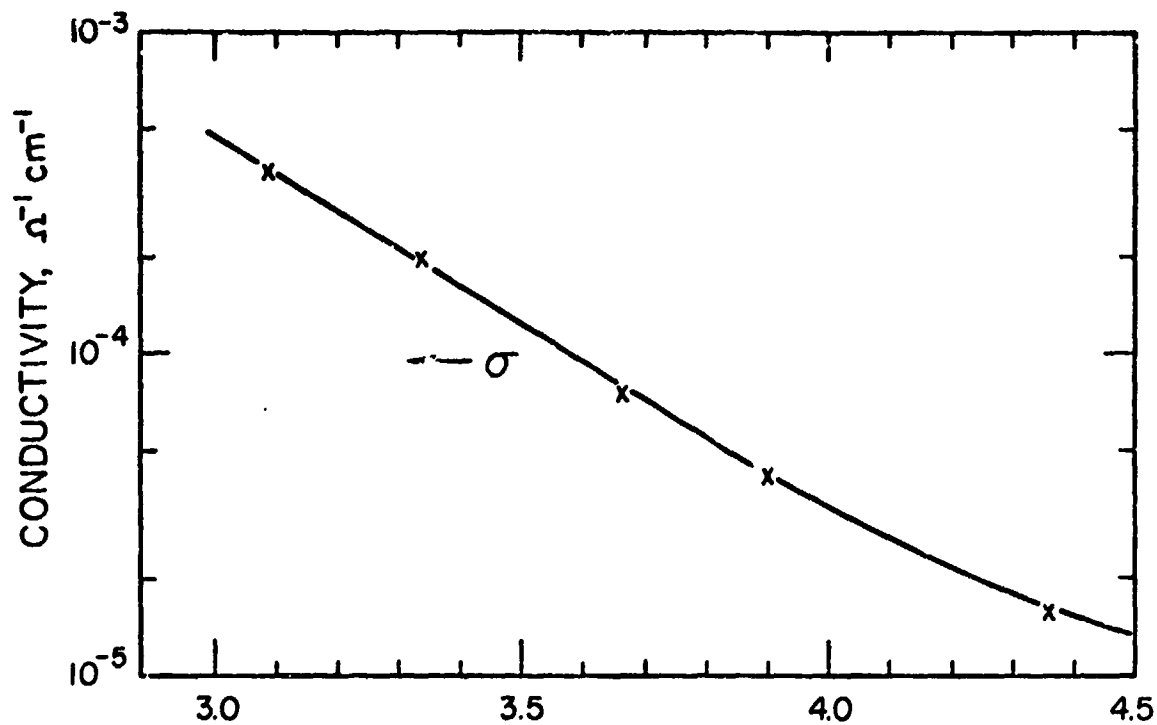
FIGURE CAPTIONS

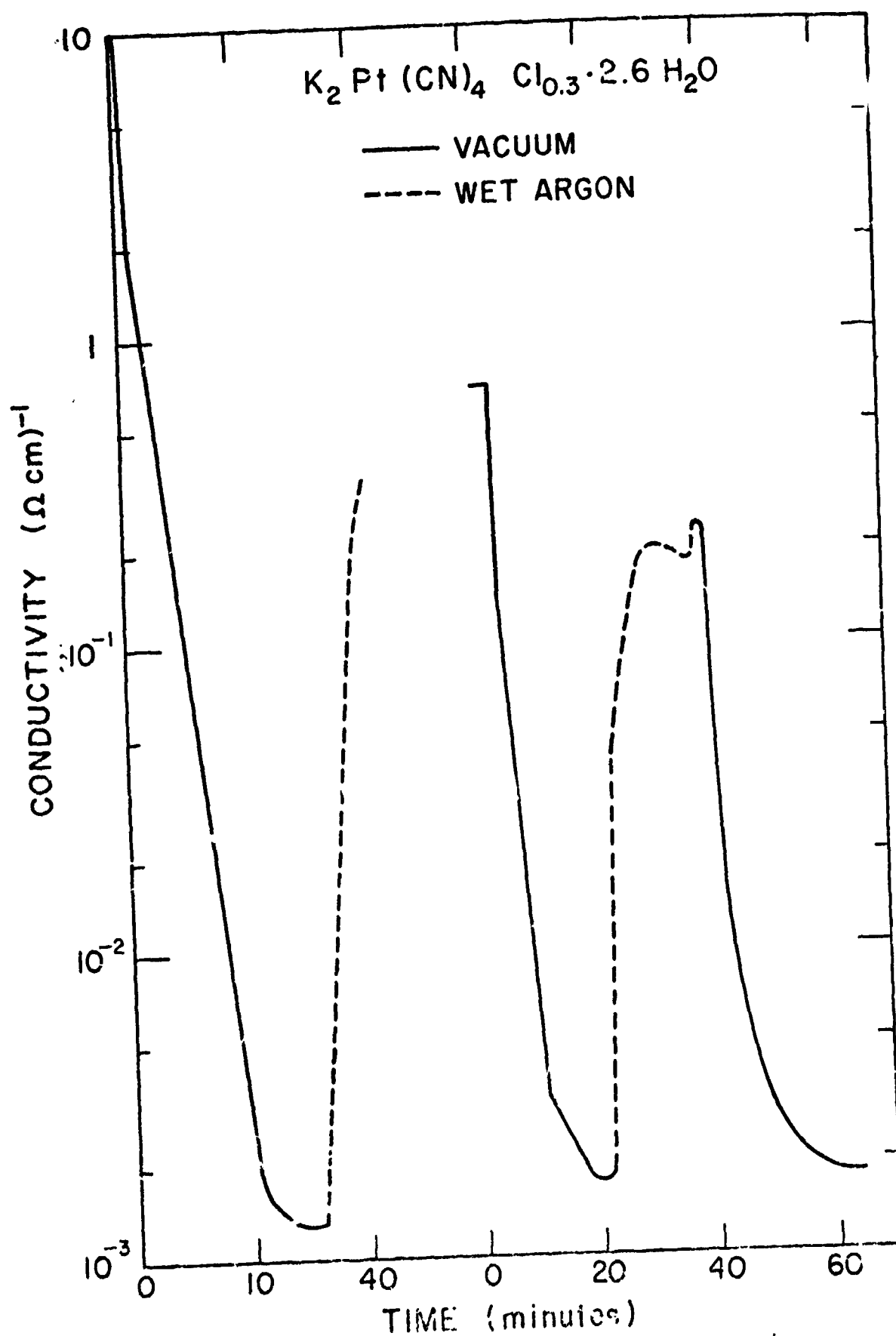
Figure 1. Temperature dependence of the four-point electrical conductivity, and of the results for hole density and mobility from analyzing thermoelectric power according to a semiconductor model, for $\text{Ir}(\text{CO}_3)\text{Br}$.

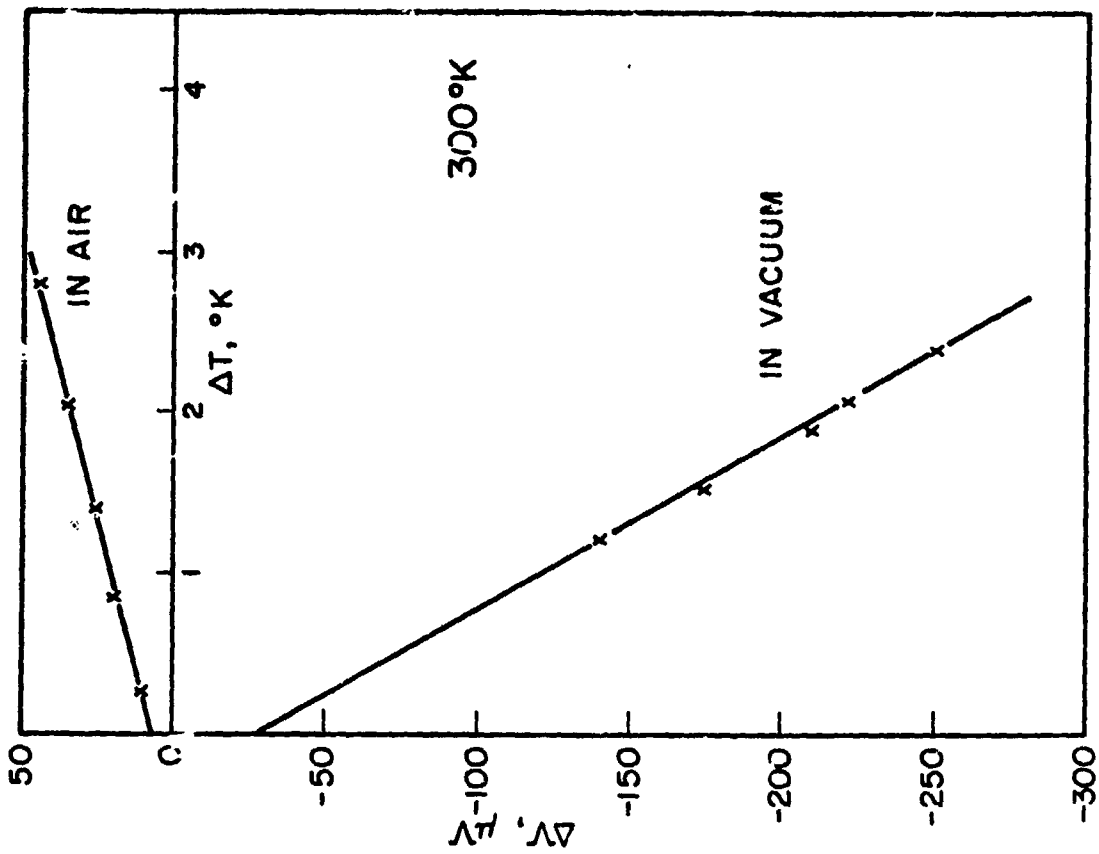
Figure 2. Variation of four-point electrical conductivity parallel to the Pt chains with relative humidity of the atmosphere, for $\text{K}_2\text{Pt}(\text{CN})_4\text{Cl}_{0.3} \cdot x\text{H}_2\text{O}$ at 300°K . A 12 hr period in wet argon occurred during the break in the curve.

Figure 3. Variation of thermoelectric voltage with temperature difference on $\text{K}_2\text{Pt}(\text{CN})_4\text{Cl}_{0.3} \cdot x\text{H}_2\text{O}$. (a) For several temperatures near room temperature, measured successively from low temperatures to high. (b) Steady values in "wet" state in air, and in "dry" state in vacuum.

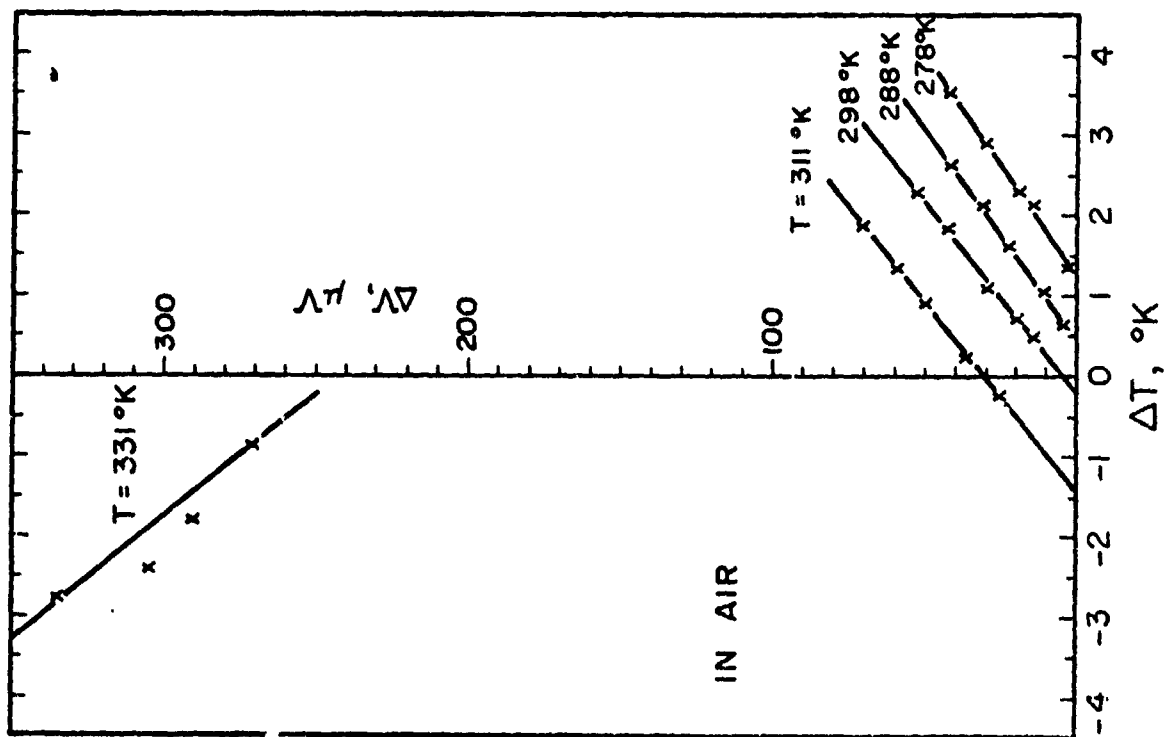
Figure 4. Temperature dependence of the four-point conductivity measured parallel to the Pt chains in $\text{K}_2\text{Pt}(\text{CN})_4\text{Cl}_{0.3} \cdot x\text{H}_2\text{O}$, for crystals protected by oil in the "wet" state, and exposed to vacuum in the "dry" state, and for data by Kuse and Zeller on $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3} \cdot x\text{H}_2\text{O}$. (a) \ln conductivity vs $1/T$, and (b) \ln conductivity vs. $1/T^{1/2}$.



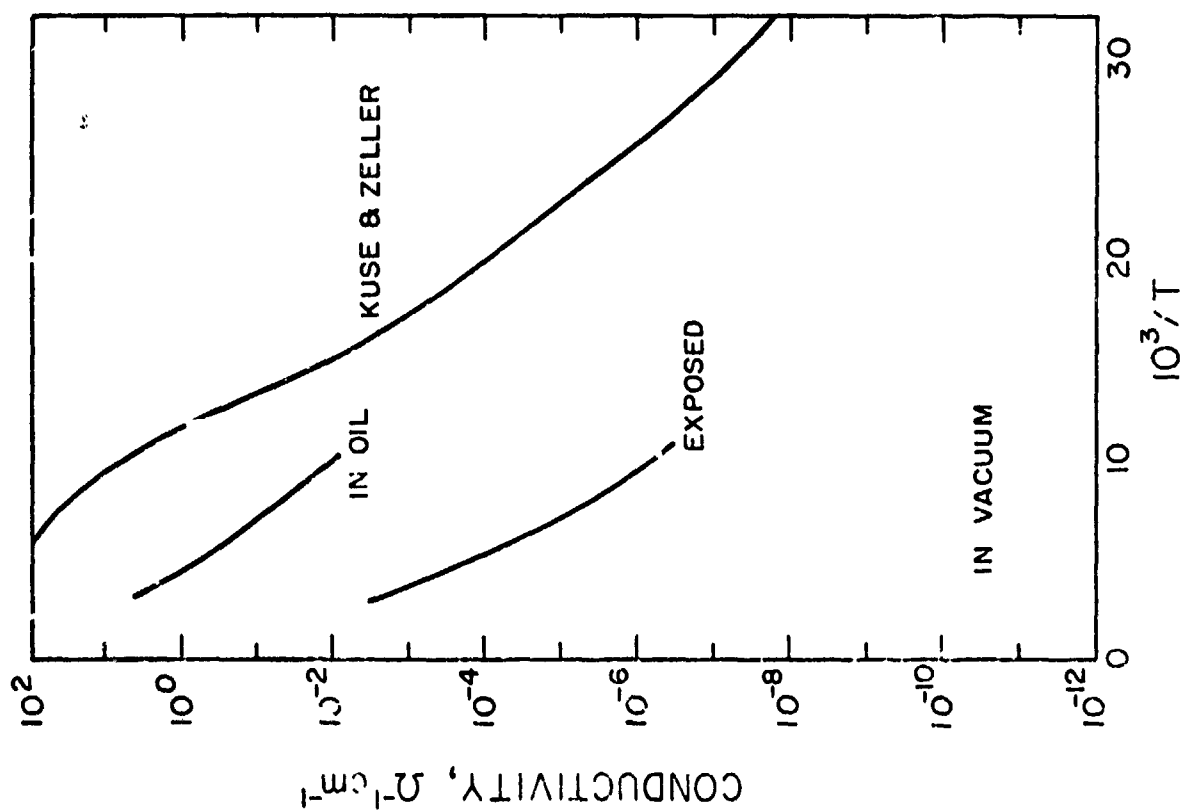
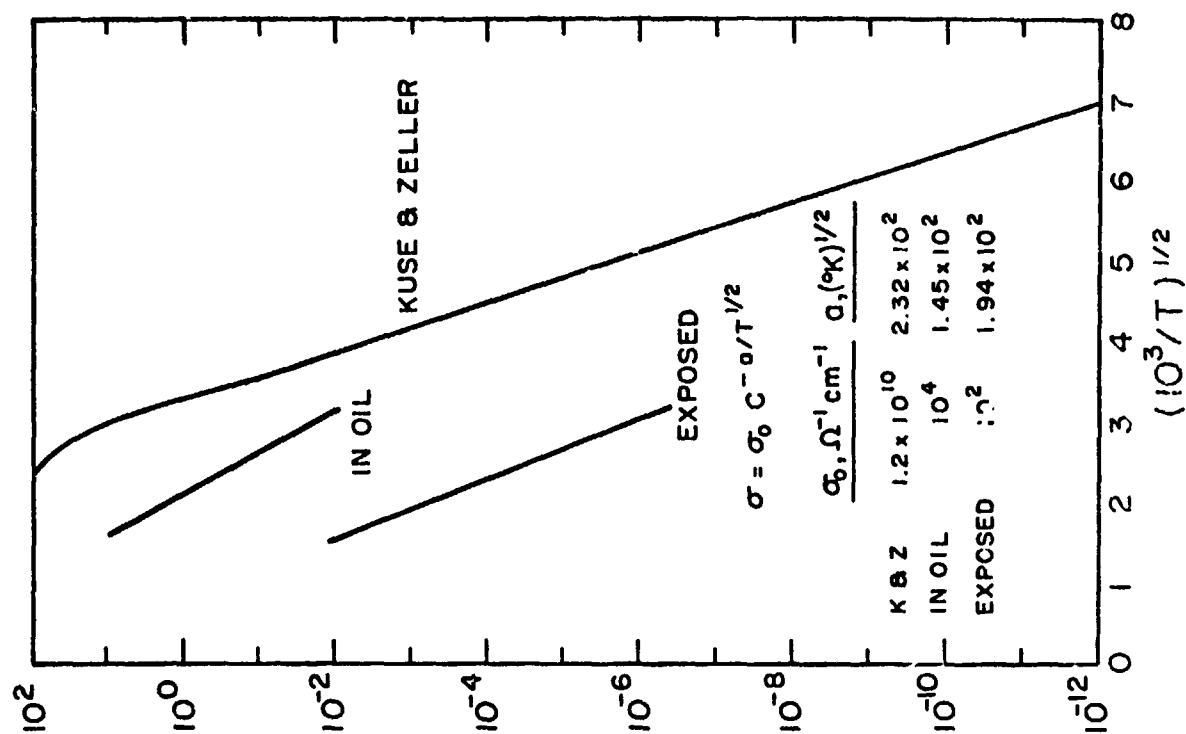




(b)



(a)



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